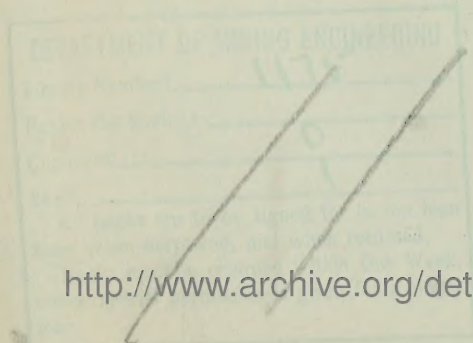


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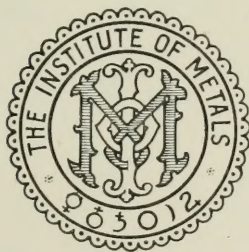
VOLUME VIII

EDITED BY

G. SHAW SCOTT, M.Sc.

SECRETARY

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THE INSTITUTE OF METALS

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THE INSTITUTE OF METALS

SECTION I.

MINUTES OF PROCEEDINGS.

MAY LECTURE.

AT a GENERAL MEETING of the Institute held at the Institution of Mechanical Engineers, Storey's Gate, Westminster, S.W., on Friday, May 10, 1912, Professor W. GOWLAND, Assoc.R.S.M., F.R.S., President, in the chair, there was delivered the third May Lecture by Sir J. ALFRED EWING, K.C.B., F.R.S.

The Minutes of the Annual General Meeting, held in London on January 16 and 17, 1912, were taken as read, and were signed by the Chairman.

Sir ALFRED EWING then delivered his lecture on the subject of "The Inner Structure of Simple Metals," a full report of which will be found on pages 4-34.

VOTE OF THANKS TO SIR ALFRED EWING.

The PRESIDENT proposed, and the Rt. Hon. Sir J. H. A. MACDONALD, P.C., K.C., K.C.B., seconded, and it was carried unanimously, that a hearty vote of thanks be given to Sir ALFRED EWING for his lecture.

ELECTION OF MEMBERS.

The SECRETARY read the following list of names of candidates who had been duly elected Members of the Institute:—

Election of Members

NAME.	ADDRESS.	QUALIFICATION.	PROPOSERS.
Allen, Thomas James Wigby	German Silver Works, Spring Hill, Birmingham	Metal Manufacturer	John H. Allen. J. W. Earle. G. A. Boeddicker.
Boote, Edgar Mid- dleton	2 Lithos Road, Hampstead, N.W.	Chief Chemist to London General Omnibus Co., Ltd.	G. B. Brook. W. R. Barclay. P. Longmuir.
Bradley, Benjamin	Dunston Metal Works, New- castle-on-Tyne	Managing Director, Bradley Ore Treatment Co., Ltd.	A. S. Esslemont. J. Adamson. A. Carter.
Cowan, George Dunford	Bridge House, Bridge Road, Millwall, E.	Manager, Lead Desilverising Works	H. C. Lancaster. T. Girtin. G. T. Holloway.
Dawlings, Richard Maurice Neave	85 Teignmouth Road, Brondes- bury, N.W.	Departmental Man- ager, Johnson, Matthey & Co., Ltd.	George Matthey. A. J. Webb. E. V. Jarry.
Garland, Herbert	P.O. Box 417, Cairo, Egypt	In charge of Egypt- ian Government's Laboratory, &c.	W. Gowland. J. T. Milton. R. Kaye Gray.
Gem, Evelyn Percy	G. Johnson & Co., Montgomery Street, Spark- brook, Birming- ham	Brass and White Metal Manufac- turer	Sir G. Muntz. R. M. Sheppard. T. Turner.
Gordon, Joseph Gordon	Queen Anne's Man- sions, S.W.	Managing Director, The Ducktown Copper Co.	S. O. Cowper- Coles. G. T. Holloway. H. M. Ridge.
Heusler, Friedrich, Ph.D.	Dillenburg (Hes- sen-Nassau), Germany	Direktor der Isa- bellenhütte	J. H. Heap. R. H. Haggie. C. O. Bannister.
James, Garnet Wil- liams, M.A., F.I.C.	Metallurgical Lab- oratory, King's College, London	Analytical Chemist	A. K. Hunting- ton. G. T. Holloway. T. Turner.
Lambert, Arthur Reginald	Mitsui & Co., Ltd., 34 Lime Street, E.C.	Buyer and Seller of all Metals for Mitsui & Co., Ltd.	A. H. Barnard. H. Kaye. A. C. Claudet.
Little, Arthur Dehon	93 Broad Street, Boston, Mass., U.S.A.	President, Ameri- can Chemical Society.	W. M. Corse. W. Gowland. W. Rosenhain.
MacIntosh, James Rae, B.Sc.	Siemens Bros. Dyn- amo Works, Ltd., Central House, Birmingham	Electrical Engineer	G. A. Boeddicker. J. H. Allen. A. Titley.
Narracott, Ronald William, D.Sc.	British Mining & Metal Co., Ltd., 123-7 Cannon Street, E.C.	Metallurgist and Engineer	J. H. Heap. G. T. Holloway. R. H. Haggie.
Nead, John Hunter, B.S.	H. H. Franklin Manufacturing Co., Syracuse, N.Y., U.S.A.	Metallurgical Engi- neer	H. M. Howe. R. R. Abbott. A. E. Seaton.
Olsson, Martin Campbell	6 St. Helen's Place, E.C.	Engineer	A. Jacob. J. T. W. Eche- varri. R. Seligman.

NAME.	ADDRESS.	QUALIFICATIONS.	PROPOSERS.
Schleicher, Aladar Paul, Ph.D.	Mérleg-utca 11 I., Budapest, V. Hungary	Metallurgical Engi- neer	W. M. Guertler. W. Gowland. W. Rosenhain.
Smith, Sir William Edward, K.C.B.	10 Hillbury Road, Balham, S.W.	Naval Constructor	J. T. Milton. H. A. Ruck-Keene. C. Buchanan.
Tucker, Alexander Edwin	55 Station Street, Birmingham	Metallurgist	W. Rosenhain. Sir G. Muntz. G. A. Boeddicker.
Wainwright, Thomas George	Fern Lea, Stocks Lane, Staly- bridge, Man- chester	Metallurgical Student	E. L. Rhead. H. C. H. Car- penter. J. H. Andrew.
Whiteley, William (Student)	22 Myrtle Terrace, Sowerby Bridge, Yorkshire	Research Student in Metallurgy	H. C. H. Car- penter. C. A. Edwards. J. H. Andrew.
Wright, Charles William	2 Evelyn Street, Deptford, S.E.	Chemist, Defries Limited	Ernest A. Smith. C. H. Wilson. W. H. Dyson.

The proceedings terminated at 10 o'clock P.M.

1912 MAY LECTURE.*

THE INNER STRUCTURE OF SIMPLE METALS.

BY SIR J. ALFRED EWING, K.C.B., LL.D., F.R.S.

IN attacking the question of what is the inner structure of metals, the microscope is our principal weapon of research. During the past twenty years or so it has taught us much about simple metals, much also about the constitution of alloys. But its powers are limited, and we find ourselves brought up against an absolute barrier beyond which the microscope cannot go. We want to know what are the ultimate particles of which a metal is composed, how these particles are arranged, and why they so arrange themselves. To these questions the microscope is unable to give us anything like a complete answer; and when we attempt to penetrate beyond the region in which we can accept it as a guide, we do so only by the help of such light as may be perceived by the eye of the scientific imagination.

My intention to-night is first to remind you briefly of some of the things that the microscope has taught us regarding simple metals, and then to go on to some more or less speculative considerations based on that knowledge. I propose to confine myself definitely to simple metals—that is, metals which behave as pure metals behave, leaving untouched the large and complicated subject of the alloys. Alloys present complexities that would only distract attention from the particular points which I wish to bring before you. Without those complexities we shall find the matter difficult enough.

Some apology is due to the experts in the audience for presenting facts with which they are already familiar, but probably the audience includes some who are not experts, and in any case it is convenient to recapitulate a little of our positive knowledge before entering the region of speculation.

* Delivered May 10, 1912, at Westminster.

Generally speaking, when we wish to apply the microscope to the examination of metallic structure, we begin by polishing the surface of the metal so as to remove those inequalities which would embarrass the use of the microscope, especially at high powers. As Dr. Beilby showed in the admirable May Lecture* he gave last year, the process of polishing itself affects the constitution. It makes the metal on and near the surface entirely different in character from the metal within. It produces, according to his view—which, I think, is now generally accepted—an amorphous layer in contradistinction to the crystalline structure which, as we shall presently see, is revealed when that amorphous layer is removed. Consequently what we have first to do after polishing is to remove the superficial layer before we can really see the normal characteristics of the structure, and the usual manner in which that layer is removed is by a light chemical attack, a slight etching with an acid or some other substance. Occasionally we may resort to other means of removing the layer. An interesting method which is sometimes available is to heat the metal sufficiently to make the surface layer sublime away.

When we lightly etch the surface of a metal, what do we see? In general we see an appearance such as is illustrated in Fig. 1, Plate I. This is a photomicrograph taken by Dr. Rosenhain of part of the surface of a bar of Swedish iron, magnified 150 diameters. A very similar appearance is presented by other metals. The surface is seen to be composed of a large number of separate grains, irregular both in size and shape, and also irregular as regards the character of the boundaries. Sometimes these are straight and sometimes curved. The shapes of the grains are as irregular as the counties in a map of England; their boundaries depend, like those of the counties, on historical conditions, as we shall see by and by.

Suppose now that we carry the etching a little further (Fig. 2, Plate II.). We discover that the grains can be distinguished not merely by these irregular boundaries. A difference of texture begins to manifest itself between one

* G. T. Beilby, "The Hard and Soft States in Metal," *Journal of the Institute of Metals*, No. 1, 1912, vol. vii. pp. 5-43.

grain and another; some grains are very bright, some are more or less dark, and some are very dark. If instead of illuminating the surface directly from above, as is the case in Fig. 2, we throw the light from one side, we discover that the same grain which appears bright under one condition of illumination becomes dark under another. Compare Fig. 3, Plate II., with Fig. 2.

These are two photographs, for which I am indebted to Dr. Rosenhain, showing the same part of the surface of one metal* under two different conditions of illumination. In Fig. 2 the light comes directly from above; it strikes the surface perpendicularly, and is reflected up into the microscope. In Fig. 3 the same grains are illuminated by light coming from one side. It will be observed that there is no difficulty in identifying the same grains in both; and that grains which are very bright under the first illumination become dark under the other. If we move the source of light to another side, or turn the specimen round, so as to alter the direction from which the light falls upon it, we find the grains vary in brightness in the most remarkable manner, sometimes flashing out brilliantly and sometimes becoming almost entirely dark. This is true of all metals. These photographs are of iron, but we find gold, silver, copper, lead, and so forth, exhibiting precisely the same general characteristics.

Examination of the etched surface under a high power shows that this difference of texture is really due to a multitude of little facets or tiny plane surfaces in each grain which are causing the general surface of the grain to reflect light in a particular manner. They are acting like a multitude of little mirrors all facing one way. These facets are parallel in any one grain, but have different inclinations in the different grains.

In Fig. 4, Plate III.,† we have a photograph of a grain of iron, not very deeply etched. A part of a single grain occupies nearly all the photograph under a power of 800 diameters. You observe that over the grain, here and there, are a number of pits which are clearly geometrical in form; they happen to

* Nearly pure iron (transformer sheet steel) annealed in hydrogen and deeply etched with copper-ammonium chloride. Magnification, 100.

† Ewing and Rosenhain, "The Crystalline Structure of Metals," *Philosophical Transactions of the Royal Society*, vol. cxliii., 1899.

be nearly square in this particular case. In some places a number of pits have run together forming a black irregular patch, but in other places you can see the individual pits quite clearly. These pits are formed in the process of etching.

Under more favourable conditions, with deeper etching, the whole surface becomes covered with such pits. Fig. 5, Plate III., is a photograph published a good many years ago by Dr. Stead,* which shows very clearly what it is that gives rise to what I have called the texture of the grain. In the former example you had only isolated pits, but in this one the appearance is such as would be presented if we were to take a great mass of brickwork and pick out the superficial bricks all over it, so as to reveal the character of the structure as built up of brickbats. That, in effect, is what happens in the etching of a metal.

I do not know any example which gives a clearer indication than this does of what causes the difference of texture in the surface of these grains, nor one that indicates more plainly the real nature of their structure, as developed by etching. One can see unmistakably how the surface of the grain consists of a multitude of geometrically similar pieces, parallel to one another, so that their corresponding facets are all oriented one way. They are oriented in different ways as we pass from grain to grain, but in any one grain they face one way, and in consequence of that the light which falls on the grain is reflected in a perfectly uniform manner over the whole expanse of that grain, although it is reflected in a very different manner from the surface of any other grain. Over each grain the brightness is uniform, because the little surfaces are acting equally as regards the reflection of light.

From this it is an easy step to infer that throughout the whole volume of any one grain there is an assemblage of pieces, which we may think of as the "brickbats" or structural units that build up the grain, all facing one way in the one grain, but facing different ways in different grains. Fig. 6, Plate IV., is another example, a piece of etched tin-plate,†

* J. E. Stead, *Journal of the Iron and Steel Institute*, 1898. The specimen is iron containing $4\frac{1}{2}$ per cent. of silicon in solid solution, deeply etched.

† Ewing and Rosenhain, *Philosophical Transactions of the Royal Society*, vol. cxcv., 1900.

exhibiting the same characteristics. It shows a portion of two grains of the thin layer of tin with the boundary between them, and the difference of brightness is very marked. They are both exposed to the same light, but they reflect different amounts into the microscope. The reason is that the little facets on one are much more favourably directed for the purpose of reflecting the light back to the microscope than are the facets on the other.

One might multiply illustrations all pointing to the same fact, namely, that the etching has revealed a definite geometrical structure within the grain by removing, as it were, a few of the superficial brickbats, leaving cavities and protuberances of a geometrical form. The conclusion is simply this, that every one of these grains is in reality a crystal. Notwithstanding the irregularity of the boundary it has the true property of a crystal, the uniformity of internal structure which is the characteristic of a crystal. It is, to use Kelvin's phrase,* a "homogeneous assemblage" of structural units which is put together with greater regularity than any structure built up of definitely formed brickbats.

In some cases we may, without etching the surface, obtain other evidence of the truly crystalline nature of the grains that make up a piece of metal. The next photograph is that of a metallic surface which has never been polished, and never been etched. It is a specimen of cadmium cast against a very smooth surface of glass so that polishing and etching might be dispensed with. The irregular boundaries of the grains are visible in the microscope, and a slight difference of texture between one grain and another may be discerned in the cast surface without any etching at all. Fig. 7, Plate IV., shows a small part of the surface under a high power, and from it we can see how the difference of texture comes about as a result of certain peculiar markings on some of the grains. Here there are two or three grains only in the field; observe that scattered over them there are little geometrical pits which have been formed in the process of casting. These pits are due to an accidental inclusion of

* Kelvin, "The Molecular Tactics of a Crystal," *Baltimore Lectures*, p. 602; see also his papers on the "Molecular Constitution of Matter," *Collected Papers*, vol. iii.

particles of gas between the metal while it was solidifying and the smooth glass surface on which it was cast. Whether that gas was air, or gas dissolved in the metal and given out in the process of solidification, I cannot say, but there is no doubt that these pits are formed by little gaseous particles. They are, in fact, negative crystals. The meaning of them is that the whole of the grain is a crystal, and these markings are only the places where the little brickbats have been left out.

Fig. 8, Plate V., is another specimen of cadmium, also cast against a smooth glass surface, showing in a beautiful manner the same geometrical air-pits. This is only a small portion of a single grain; and it may be regarded as rather a *tour de force* of microscopic photography, having been taken under a power of 4200 diameters. The geometrical markings are pits, not excrescences standing up from the surface.*

The real nature of the grains, then, is that they are crystals, and I think it may make the matter more intelligible if we try to think of the process of crystal building which has resulted in the formation of these grains. How does it come about that the external forms of the grains are so different from the simple, symmetrical forms which we are accustomed to find in isolated crystals? The reason is this. These crystals have grown more or less simultaneously from a number of different centres of crystallization. The metal as a whole is the joint result of much independent building, such as we might compare to the building of toy bricks by a number of children in a nursery. Suppose we had a number of little fairy children—I say fairies in order that they may be able to disappear as the structure completes itself—a number of fairy children provided with an unlimited supply of perfectly similar brickbats. Place them all over the nursery, not only on the floor, but throughout the volume of the room, and let them start building, not necessarily simultaneously, but capriciously as regards time, and capriciously also as regards place and as regards the positions in which they put down their first brickbats. What would be the result? As each fairy child puts down its first brickbat and goes on adding one to another, a crystal grain will be built. Some may build more

* Ewing and Rosenhain, *Philosophical Transactions*, vol. cxiii., 1899.

quickly than others. What is it that will determine the external form? Simply that each will go on building until the territory is entirely occupied, until the structure which each child is erecting is limited by being brought into contact with the structures of the neighbours. That is precisely analogous to the process that occurs in the solidification of a metal. One may carry the analogy further by thinking of some of the fairy children as having a genius for colonization, because they stretch out lines which secure for their own building a comparatively large share of territory. Having stretched out these long branching lines, they then proceed in a leisurely manner to fill up the gaps. This is an example of what is called in crystallography dendritic growth. It is a common kind of growth in the actual formation of a solid metal.

In most instances of metal structure, the grains of which the metal is composed are so small that to see them clearly requires the use of the microscope, but under favourable conditions we may have comparatively large grains. There is an example here of a specimen of cast lead which was prepared in my laboratory at Cambridge by Mr. Humfrey some years ago in connection with a research which he was then making on the structure of lead.* It has grains so large that some of them measure two or three inches across. The piece is lying in dilute nitric acid, which has had the effect of etching the surface and leaving it exceedingly clean, and as I turn it round under a beam of light from the lantern, you will see that the grains darken and flash out bright according to the orientation of the little mirror-like facets of which the etched surface is composed. As a rule we require a microscope magnifying 100 times or more in order to obtain reasonably good photographs of the grains in a metal, but these exceptionally big grains need no enlargement.

Occasionally we find examples of dendritic growth on a large scale in iron castings. Mr. J. T. Milton has been kind enough to send to-night a beautiful specimen of this, a piece cut out of the pipe of a large steel casting showing the crystals in which the metal originally settled itself, dendritic in form.

* J. C. W. Humfrey, *Philosophical Transactions*, vol. cc., 1902, p. 225.

resembling very regular pine trees, and with undisturbed geometrical outlines, resulting from the fact that while those crystals were still growing the liquid metal round about them was drained away by the contraction of the casting below.*

Sometimes evidence of dendritic growth is seen even upon a free surface of a solidifying metal. A dendritic skeleton forms first in the solidification of the surface layer, and this is subsequently thrown into relief by the irregular contraction that results from the cooling of the later growth. Fig. 9, Plate V., shows a case in point: it is part of the free surface of antimony solidified after melting.

I cannot well exhibit the process of crystallization going on in an actual metal, but substantially the same thing is readily shown in the lantern by using a salt in solution, which deposits crystals in the same way as they are formed in the solidification of a liquid metal. Take, for example, a solution of sal ammoniac, and, in order not to spend too much time over the experiment, warm it up so that it dissolves some more of the salt, and then run a little of it over a glass plate so as to leave a thin film on the plate. The plate is now put in the lantern, and you see crystallization begins almost at once. Here we have, as it were, the nursery floor, not the whole volume of the room, and the fairy children are getting to work; they are beginning, some at the edge and some more or less in the centre. Grains are forming at a number of places, and are spreading until they meet. Soon the whole plate is covered with them. I want you to notice how the shape of each is conditioned simply by its meeting neighbouring grains. Each grain is a true crystal, though its final shape is quite irregular. Those of you who are near enough will be able to see that the early stages of the growth of a grain are of the dendritic type; it throws out branches forming a skeleton which is afterwards filled in.

A very important point about metallic structure is that we find true crystal grains not only in metals in the cast state but also in metals in other states, metals which have been wrought, which have been shaped by working even in the

* A fine example of this dendritic structure in a steel casting is shown by Mr. E. F. Lange in the *Proceedings of the Manchester Literary and Philosophical Society*, vol. lv., 1911.

cold condition, and also in metals that have been worked in the cold condition and have afterwards been annealed by bringing them to such a temperature that a rearrangement of the grains has taken place. Whether we deal with them in the cold condition or in the annealed condition, we still find the same general characteristics, still the same granular structure, and still the same plain evidence that each grain is in reality a crystal.

Take, for instance, a bar that has been shaped by being passed through a rolling-mill in the cold state. One of the photographs already shown (Fig. 4, Plate III.) is part of the transverse section of a cold-rolled iron bar, rolled down from a comparatively large diameter, so that the individual grains within the bar have suffered tremendous distortion in the process of rolling. The greater part of the field is covered by a single crystal. Over its whole surface there are geometrical pits. When it was examined very carefully in the research by Dr. Rosenhain and myself* we found that these pits were parallel all over the crystal notwithstanding the tremendous distortion it had undergone. It was clear, therefore, that the regular parallel grouping of the structural units or brickbats had in some way or other been preserved during the process of severe straining.

The point is further illustrated if you examine in the microscope a specimen of metal that has been broken in a testing machine. Take a fairly plastic metal, such as iron or mild steel, which stretches a good deal before it breaks. If you polish and etch the side of the bar near the fracture, where a considerable amount of extension has taken place, you will find that the metal there consists of grains similar to those you have already seen, but with this difference, that these grains are all elongated in the direction of the stretching. Their shapes may be still very irregular, but there is clearly a predominating greater length in the direction along the bar, as compared with the transverse direction. The stretching the specimen underwent before it broke has elongated each grain, but its granular character persists.

* *Philosophical Transactions*, vol. xciii., 1899, pp. 366-367.

The crystalline constitution of the grains, then, survives severe straining. How does it do so? That is a question Dr. Rosenhain and I set ourselves to answer. We tested specimens of metal by straining them actually under the lens of the microscope and observing what happened during the process. The specimen was a thin strip of sheet metal, which was strained in such a manner that the same crystals were kept in view the whole time. In Fig. 1, Plate I., we had a specimen of iron lightly etched. This was subsequently strained by tension, but the photograph of Fig. 1 was taken before the straining began. In Fig. 10, Plate I., we have identically the same grains after a slight amount of straining—enough to carry it beyond the elastic limit, but not much beyond. If we compare those two accurately by applying compasses and measuring the lengths of the grains, it will be found that in Fig. 10 each grain has become a little stretched in one direction and a little shortened in the transverse direction. But that is not the main difference. The main difference produced by the straining is that over the surface of each grain a number of curious black lines have appeared, almost like the crevasses of a glacier, lines which are substantially straight and substantially parallel. It is in virtue of these lines that the plastic strain of the crystal grain has happened. These lines mean not that crevasses are formed, for there is no rupture of continuity, but that there has been shearing at a corresponding number of internal surfaces, that the crystal grain has behaved as a pack of cards behaves when you try to make it alter its form. The pack of cards becomes strained by the slipping of one card on the other, of each layer on its neighbour. In precisely the same way the crystals of metal become strained by the slipping of the little brickbats of one layer on those of the adjacent layer within each grain. The result is that on the polished and etched surface little steps are formed by the slipping, and it is these little steps that constitute the black lines you are now looking at. They are narrow bands rather than lines; Dr. Rosenhain and I, when first we discovered them, called them “slip bands.” *

* Ewing and Rosenhain, *Proceedings of the Royal Society*, vol. lxxv. p. 85; *Philosophical Transactions*, vol. cxciii., 1899, p. 353.

Perhaps you will realise the nature of these lines better by looking at another specimen of strained metal. Fig. 11, Plate VI., shows under a power of 60 diameters a specimen of lead in which one got a beautifully smooth surface, and then severe straining brought out the slip bands or slip lines. I compared the action just now to that which occurs in a pack of cards, but the comparison is a very incomplete one. In order to admit of the changes of form that are brought about by straining, one must have slips not only on one system of planes, but on several systems—on three systems at least in each grain in order to get such complete distortion as may occur. It will be noticed in Fig. 11, Plate VI., that in some of the grains four distinct systems of slip lines are visible. These have been carefully traced, and it has been found that they represent slips on the four octahedral planes of the cubic crystals of which the lead is composed.

The process which I have attempted to describe may be illustrated by a very rough diagram (Fig. 12). This is an

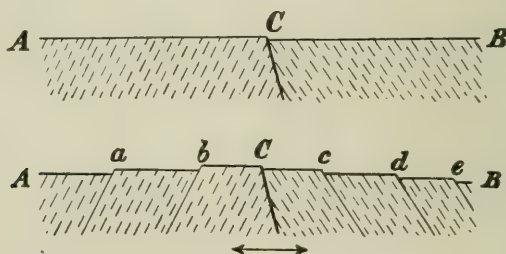


FIG. 12.

imaginary section through a couple of crystal grains. The line at the top represents the polished surface which we are looking at from above in the microscope, AC being part of the surface of one crystal grain, and CB that of another. The dotted lines represent the manner in which the layers of brickbats are disposed in the two crystals. Now, imagine that straining takes place so as to stretch the whole thing in the direction AB; the result is that every here and there in the crystal CB slips will take place (as at *c*, *d*, and *e*), the part to the right slipping down relatively to the part to the left.

Similarly in the crystal AB slips take place at a and b , the part to the left slipping down relatively to the part to the right. In consequence of that you get a number of steps formed on the polished surface. One such step has been formed at a , another at b parallel to it, and so on. When you look at the surface through the microscope, throwing the light directly down upon it, the light which falls on those parts of the surface between the places where slip has occurred is reflected up again into the microscope, and those parts accordingly appear bright, but the light which falls upon any one of the little sloping steps is reflected away, and therefore each step appears in the microscope as a narrow dark band.

Clear proof that the slip lines are really little steps was furnished by testing the effect of oblique illumination. It will be obvious that, if the theory is correct, it should be possible, by throwing the light from the side, to get the little step which was dark in the first instance to shine up brightly. We have only to choose an appropriate direction from which the light should come in order that the step may reflect it up into the microscope. That has been done in this slide. Here are illustrations of what Dr. Rosenhain and I found when we made that experiment. In Fig. 13, Plate VII., we have several grains of a strained specimen of lead illuminated by light falling very obliquely from one side. The light is so placed that some of the slip lines or slip bands are bright, through reflection from the little steps up into the microscope. The light is falling on all the grains alike, but only one is visible, because none of the slip lines on the others are favourably situated for reflection into the microscope. Now we shift round the direction of the illumination (Fig. 14, Plate VII.): another crystal has its slip lines brilliantly illuminated, and at the same time the one that had its lines illuminated before has now become dark.

Fig. 15, Plate VI., is a photograph of the system of slip lines on a small part of a single lead crystal under a magnification of 1000 diameters. You can see that the slips have produced small differences of level, and it is apparent that they have taken place successively in the different planes, so as to result in a compound system of steps.

Dr. Rosenhain gave subsequently a further demonstration by obtaining a transverse section of the steps formed by slipping. To do this he strained a piece of iron to form the lines, and then deposited a thick layer of copper upon it by an electrolytic process; finally he cut a transverse section through both the iron and the copper covering, and polished that for microscopic examination. Under a high power it was seen that the surface between the two metals had upon it a number of little definite parallel steps, which corresponded to the slip lines produced by straining the iron.*

We conclude, then, that the plastic yielding of metals under strain is due to slips occurring on the gliding planes of the crystal grains. This notion gives a key to plasticity in metals. It is not going too far to say that any amount of distortion can be accounted for by slips of this kind without requiring the continuity of the crystalline structure to be interrupted.

I do not say that there is not some disturbance of the particles in and close to the plane of slipping. Dr. Beilby has suggested that in the process of slipping a thin amorphous layer is formed as one part of the crystal slips upon another. The idea is consistent with the observed fact that when you have a frequently repeated succession of slips backwards and forwards you get a deterioration of the material which may ultimately result in fracture. This is the well-known fatigue of strength, caused by repetitions of straining, an immensely interesting matter about which the microscope tells us much, but to discuss it would take us too far to-night.†

A point of fundamental importance in relation to the crystalline structure of metals is the frequent presence of what are called twin forms. Twinning sometimes results as a direct effect of straining. Much more commonly it is found in a metal that has been strained and then annealed. It does not occur in all metals. It is conspicuously absent in forged iron under ordinary conditions,‡ but in gold, copper, silver, or lead you often find it when the metal is in the wrought state.

* W. Rosenhain, *Journal of the Iron and Steel Institute*, vol. lxx., 1906; also *Proceedings of the Royal Society*, vol. lxxiv., 1905.

† See Ewing and Humfrey, "On the Fracture of Metals under Repeated Alternations of Stress," *Philosophical Transactions*, 1903, vol. cc.

‡ Namely, in α -iron: in γ -iron it is frequent.

Perhaps the most intelligible way to explain what is meant by twinning is to ask you to think of the process of crystal building by the piling up of layers of "brickbats" or structural units one upon the other. Suppose that after you have reached a particular layer the units which are going to be deposited to form the next layer are not laid down parallel with those that have gone before, but that every one is turned through a definite angle, let us say 180° , about an axis perpendicular to the layer, before it is laid down. If you imagine that to happen, you will have a case of what is called twin formation; the part above the plane will be in twin relation to the part below it. Very often this happens for a certain number of layers, and then there is a reversion to the original form, and in consequence of that the surface of a cross-section, as we see it in the microscope, exhibits parallel boundaries, between which there is a band showing an entirely different texture from the material on either side, dark while the rest is light, or it may be light while the rest is dark. Whenever this characteristic appears it is to be recognised as due to twinning. Sometimes you find a series of parallel bands, each of which is a twin to its next neighbour.

By way of illustration, I reproduce in Fig. 16, Plate VIII., a photograph, published some years ago by Professor Liversidge,* showing in section an Australian gold nugget in its native state. Here the grains are comparatively large, and several of them are characterized by the presence of twins. On one of the grains you see a beautiful example where the twin does not extend across the whole grain, but is isolated on all sides. The photograph as reproduced is only a little larger than the natural size.

When we strain a twin piece we get a very interesting manifestation of its twin character by finding that there is a sudden change in the direction of the slip lines. Instead of running straight across the crystal parallel to one another, they suffer a sharp change of direction where they pass into the twin-band, and then revert, with equal sharpness, to their original direction, where they pass out of it. Fig. 17, Plate

* A. Liversidge, "The Crystalline Structure of Gold and Platinum Nuggets, and Gold Ingots," *Journal of the Chemical Society*, 1897.

VIII., is an example of twins in wrought copper which has been strained so as to develop the slip lines: notice the sudden change in their direction as they pass across the planes on which twinning has occurred. When there is a succession of parallel twin bands you get an appearance that recalls the herring-bone pattern of a parquet floor.

I have mentioned this subject of twinning at some length, because it seems to me to have an important bearing on any conjecture we may frame as to the manner in which the structure of the crystal is made up. What little time remains must be devoted to speculative consideration of the inner nature of the structure—to what Kelvin has called the molecular tactics of the crystal. We have seen that the crystal grains of metal, like any other crystals, are composed of units—units of finite size which are arranged in a perfectly regular manner. The structural units are set in rows, the rows are set in layers, and the layers are piled on top of one another. We have, as I have said, a “homogeneous assemblage,” like the well-drilled flowers on a mid-Victorian wall-paper, or like what soldiers on parade would be if all soldiers were precisely alike and were spaced with perfect exactness. What are these structural units? We do not know whether they are the molecules of the metal or whether they are aggregations of molecules, and, so far as the present inquiry is concerned, I do not think it very much matters. Even if they are the molecules, there can be no doubt that they themselves possess a somewhat complex structure. We may picture to ourselves each unit as having within itself a quality of direction so that it can be oriented in a definite way. We do not think of it simply as a uniform sphere without directional quality. It may be regarded as having externally the form of a sphere; in any case that is a convenient way of geometrically representing the fact that in crystals of the types with which we are now concerned the units are spaced in regular rows at a uniform distance apart. Whatever be the real nature of the structural units, their spacing relatively to one another is that which would be assumed by equal spheres in contact. Moreover, we have to think of the particles as being capable of turning; in that respect also they behave like spheres.

We accordingly represent the homogeneous assemblage of particles by means of balls in contact with one another. The question then arises, how may we pile spheres in contact with one another so as to build up structures that will possess those types of symmetry which we observe in metal crystals?

Before attempting to answer that question, I wish you to realise that the symmetry which is the fundamental characteristic of crystalline structure is not symmetry of external form but of internal grouping, namely, of the arrangement of the structural units amongst themselves. Symmetry of external form may, under favourable conditions, result from symmetry of internal arrangement; but you may have the latter, which is the essential thing, without the former, as, for example, in the grains of a metal where the external form is interfered with by the simultaneous growth of neighbouring grains. It is symmetry in the assemblage of the structural units that distinguishes a piece which is crystalline from one that is amorphous or non-crystalline. And it is through differences in the kind of symmetry under which the units may be assembled that we distinguish one type of crystal from another. Thus, for instance, you may assemble balls in contact with one another in more than one way, and certain of these assemblages, as we shall see presently, satisfy the condition of complete cubic symmetry, possessing 13 axes and 9 planes of symmetry, and so constituting the most symmetrical assemblage which it is possible to produce. Another somewhat different mode of assembling the balls in contact gives symmetry of the hexagonal type.

These, the cubic and the hexagonal, are the two systems of crystallization with which we are particularly concerned. Nearly all the metals belong to one or the other; and most to the cubic system. As Osmond and Cartaud have shown, iron in each of its three allotropic forms is cubic,* and so are gold, silver, copper, lead, platinum, iridium, osmium, mercury, chromium, nickel, and other metals which are less common. Among hexagonal metals are zinc, cadmium, and magnesium.

* F. Osmond and G. Cartaud, *Annales des Mines*, vol. xvii., 1900, and vol. xviii., 1900; also *Journal of the Iron and Steel Institute*, vol. lxxi., 1906.

Consider first the grouping that will give cubic symmetry, which is the highest degree of symmetry that any crystal can possess.

There are three possible ways, and three only, in which particles may be piled so as to possess this symmetry. Imagine yourself to be piling balls, such as these ping-pong balls upon the table, and to aim at securing the symmetry of a cube. The first and simplest way is to pile them so that each ball is in contact with six neighbours. Take, for instance, a layer of balls put together as in Fig. 18, and put another exactly similar layer over it, ball upon ball, and another layer over that, and so on. You get in that way the simplest mode of piling with cubic symmetry, and also the most open mode

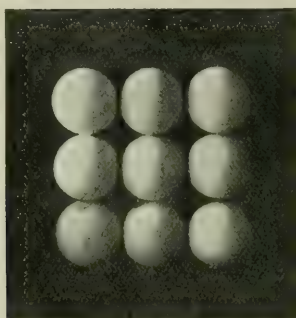


FIG. 18.

you can possibly have. In this case, when you extend the group indefinitely, you find that each ball is in contact with six others. Or you may take a more intimate mode of piling, in which each ball is in contact with eight others. Here is an example of it (Fig. 19), where for the sake of clearness I have painted half the whole number of balls red, and left the others white. When you come to look at this model you will see that inside the eight red balls there is one white ball, and inside the eight white balls there is one red ball; and similarly if we went on piling them we should find that every red ball had eight white ones touching it, and every white ball had eight red ones touching it. In this mode of piling, which also satisfies cubic symmetry, you have each ball in contact with eight others.

Now we come to another mode much more interesting than either of those, the mode which yields the closest packing we can get with spherical balls, in which each ball is in



FIG. 19.

contact with twelve others. Suppose that you take one ball, A (Fig. 20), and place four balls in contact with it as shown in the figure, and take four others as at B, and lay those four

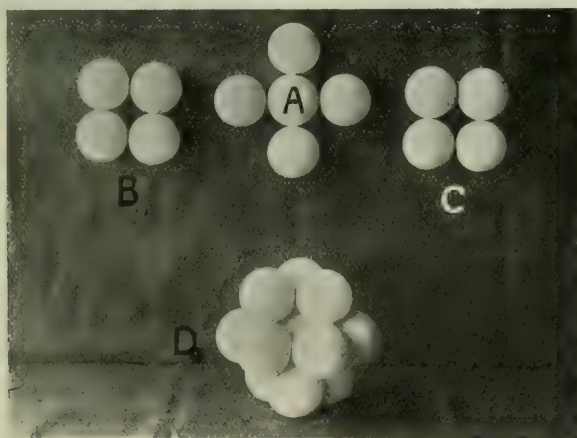


FIG. 20.

on top of the first group in such a manner that all four come into contact with the ball A. Then take another four (C), and put them below the first group so that they also all come

into contact with the ball A. You will have a pile resembling a mulberry as at D, in which the ball in the centre is in contact with twelve.

You may get precisely the same result in a different manner, which is illustrated in Fig. 21, namely by placing the balls in layers in "triangular order," so that the centres of any three contiguous balls in the layer are at the corners of an equilateral triangle, and then laying these layers on top of one another so that each ball in any one layer rests in the hollow made by three balls of the layer below. Take the first ball, and put six around it as in the central upper group in Fig. 21.

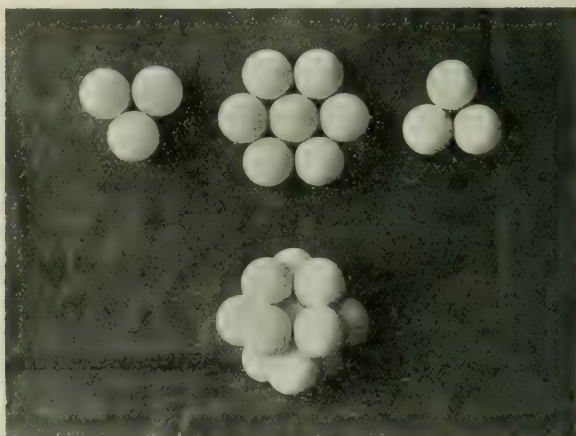


FIG. 21.

Take three others, forming an equilateral triangle, and put them below the six, so that they all touch the central ball of the first group. Then take three others, and lay them on top so that they too shall all touch the central ball. You will observe that there are two possible positions in which you can place them to do that. You can place them so that they lie parallel to the position they occupy in the figure, or you can turn the three on top round through 180° , so that each of them lies exactly *vis-à-vis* to one of the three balls which make up the bottom layer. That is a very important distinction. If we pile up our mulberry—which is precisely the same mulberry as we had in the previous case—

by placing the three layers in the manner indicated in the upper part of the diagram, we get the condition of cubic symmetry satisfied. I think this was first explicitly shown by Mr. Barlow, in one of the earliest of his important studies of the geometry of crystal symmetry.*

From one of his papers I take the next diagram (Fig. 22), to show definitely how we get the form of the cube and also the form of octahedron by piling balls in such a way as to have closest packing. Here we have layers of closely packed balls arranged in triangular order, laid as you see in a sloping position one against another, and we get the cube, as in the figure on the left. By omitting those balls which would otherwise form a corner of the cube, as in the figure

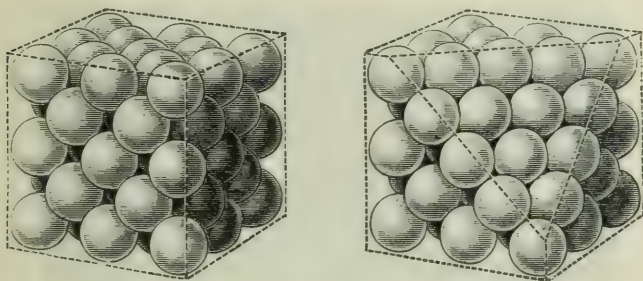


FIG. 22.

on the right, we exhibit a layer parallel to a face of the octahedron. Observe that it is on the octahedral planes that the balls lie most closely: it is on them that they lie in triangular order. It is on the octahedral planes in the cubic metals that slipping occurs, and it is on these same planes that twinning occurs.

Fig. 23 represents our two mulberries again, with the difference I indicated just now, which we get by selecting one or other of the two alternative positions for the third layer. If we place the third layer immediately *vis-à-vis* to the first layer, as in the group to the right, we get hexagonal symmetry. If we place it as in the group to the left, we have a homogeneous assemblage possessing cubic symmetry. The closeness of packing is equal in both cases. This distinction of

* W. Barlow, *Nature*, December 20, 1883.

course holds however much we extend the group by adding more balls in each layer, and by adding more layers: in the hexagonal system the balls are *vis-à-vis* in the first, third, fifth layer, and also in the second, fourth, sixth layer, and so on. You will appreciate the distinction readily if you pile actual balls; when you come to place one layer over another, you find that there are two possible situations for the balls. By choosing always those places that are not *vis-à-vis* to the balls in the last layer but one, you get an assemblage with cubic symmetry.

Confining our attention for the present to the cubic system, there are, as we have seen, three possible modes of piling; first, the most open piling with each spherical unit touching

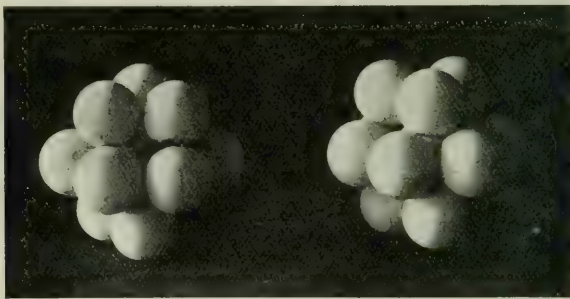


FIG. 23.

six others; second, the medium-close piling, with each unit touching eight others; and lastly the closest mode, with each unit touching twelve.

Now we come to a highly interesting question. Assuming that the structural units of the crystal behave like spheres piled in one of these various modes, what mutual forces do they exert on one another to make them fall into place and remain in place? Can we think of them as having polarity, in virtue of which each assumes its proper orientation and position? And if there are such polar forces among the structural units of the crystal, do they assist us to explain any of the known physical properties of the substance?

In an address to the Engineering Section of the British Association at York, in 1906, I attempted to suggest answers

to these questions, on the supposition that the units were grouped in the first or most open mode of piling. I showed that we should get that mode of piling if we supposed each unit to have three rectangular axes with opposite poles at their extremities, making six poles in all, three positive and three negative.* Some of the consequences were illustrated by means of a model, in which the interactions of such units were shown, the units in the model being composed of crossed magnetised bars, free to turn on fixed needle points as pivots. If there is any such polarity in the units of a crystal, it is no doubt electric, not magnetic—we may think of the unit as containing within itself a group of electrons—but it is convenient to make use of magnets in the construction of a model. They give us mutual forces of the same general character as we get with electrons, namely, attraction between unlike poles and repulsion between like poles.

A model arranged in that way shows how, as one after another molecule or unit is brought up, it takes its place as a member of the homogeneous assemblage, assuming the proper orientation as it settles down. You may disturb the assemblage by forcing any one member to turn round a bit, and then letting it go, when you see waves of disturbance passing from unit to unit. A violent disturbance may set many of the units spinning, and when they settle down again you sometimes find that they are not all homogeneously grouped, but some have taken up a position of less stability. They have formed what may be called a dissenting group, the members of which keep one another in countenance, though they are not in complete harmony with their environment. If we set them oscillating, so as to imitate the effect of raising the temperature, we may find this less stable group break up and fall into line with their neighbours. Something of this kind occurs in the annealing of a metal. One might say that Nature copies the methods of the mediæval Church in bringing dissenters to reason by the application of heat.

There are other points on which such a model throws light. We can use it, for instance, to show what happens when slipping occurs, and this we may illustrate by the single-layer model

* *British Association Report*, 1906. Presidential Address to the Engineering Section.

now in the lantern. Suppose that one portion of the crystal slides past another portion, we imitate that action by causing one group of the pivoted particles to slide past another group. Notice the effect. Across the plane of sliding the polar forces continue to act, causing first a quasi-elastic turning; but when a certain very limited range of movement is exceeded there is dissipation of energy through the original bonds being broken and new bonds established, with oscillation of the particles. The model exhibits well the essential difference between elastic and plastic strain, and shows how it is that work has to be expended irrecoverably in making a plastic strain occur.

In this model we have obtained the mechanical forces which the particles have to exert upon one another by the device of supposing positive and negative polarity within each unit. It would do equally well to take an equal number of positive and negative units—that is, a number of units in which all the six poles are positive and an equal number in which all the six poles are negative. If we jumble these up together, but give them freedom to assume their most stable grouping, they will necessarily take up the same configuration as in this model, namely, the most open mode of piling with cubic symmetry.

Again, if instead of six-pole units we were to take eight-pole units, keeping equal numbers of positive and negative units, but letting each unit have eight poles of the same name, we should find them assume the second mode of piling, the mode illustrated by red and white balls in Fig. 19.

But I am more interested in the question: What sort of polarity must we postulate in order to get the closest mode of packing? There seem many grounds for believing that it is the closest mode of packing rather than the open modes which the crystal units actually assume. It is true that Professor Sollas* favours the idea of open packing for metals crystallizing in the cubic system; and Kelvin accepted as probable alternatives all three modes, the close, the medium, and the open;† but Mr. Barlow and Professor Pope, in much of their recent work, have

* W. J. Sollas "On the Intimate Structure of Crystals," *Proceedings of the Royal Society*, vol. liii., 1898.

† See especially his "Molecular Dynamics of a Crystal," *Baltimore Lectures*, p. 672.

given what seem strong grounds for thinking that in general crystalline constitution is that of closest packing.* However that may be, let us face the problem of what arrangement of poles could produce closest packing. The first models I tried were tetrahedra with four poles. These, and also the other models which have still to be brought under your notice, are magnetic models. They are built up by taking a central boss, which may conveniently be a steel ball, screwing rods of equal length into it, with a small steel ball upon the outer end of each rod. Then the rods are magnetized, so that all the outer balls become poles of the same name, while the central boss forms a pole of the opposite name. In the first model



FIG. 24.

(Fig. 24) there are four rods and four circumferential poles, forming the corners of a regular tetrahedron; all these are south poles, while the central ball is the north pole. There is also a pivot hole drilled in the central boss, and the base board carries needle centres, which are equilaterally spaced in triangular order, and on these the little four-pole magnets are balanced, so that they turn freely under the mutual repulsion of the external poles.

They assume the configuration shown in Fig. 24, which is in fact a photograph of a single layer of such pivoted units after it has come to rest. It is a very regular configuration, but it is not consistent with cubic symmetry, because the faces

* W. Barlow and W. J. Pope, "The Relation between the Crystalline Form and the Chemical Constitution of Simple Inorganic Substances," *Journal of the Chemical Society*, vol. xci., 1907.

of the pivoted tetrahedra do not place themselves so as to be similarly related to the four octahedral planes of the system, of which the table top is one.

Suppose, however, that we introduce a new element, modifying the equilibrium. Let each structural unit be associated with what I shall call provisionally a "cementing corpuscle," namely, an isolated pole, opposite in sign to the circumferential poles of the units. If they are electrons, it is an electron of the opposite kind. Think of this "corpuscle" as finding its habitat in one of the interstices between the closely packed spheres. As soon as we accept this idea we find there is no difficulty in getting the units to pile up into most satisfactory crystals, by



FIG. 25.

placing themselves unit by unit and layer upon layer, so that they satisfy the condition of cubic symmetry.

Fig. 25 shows a small group of pivoted four-pole units, forming a single layer, in the positions which they assume under the influence of the "cementing corpuscles." These bodies are visible in the figure as isolated poles in the inter-spaces, and towards them the arms of the tetrahedra point. In the magnetic model shown in this photograph these isolated poles are obtained by using long wire magnets, of which they are the upper ends, the remainder being below the table.

In the model the pivots are at the corners of equilateral triangles, so as to simulate the conditions of closest packing. A more complete model, with two layers, is shown in Fig. 26, the upper layer being supported on a glass plate. The pivots

are omitted, but the pieces are placed in the positions of equilibrium which they would take up under the influence of the corpuscles. The corpuscles themselves are not represented in the model, but you are to imagine them as there. Each corpuscle (in an extended assemblage of the type shown in Fig. 26) occupies the centre of a tetrahedral cluster of four poles contributed by four neighbouring units, the corpuscle being of course opposite in sign from the poles, and causing the poles to point towards it.

The whole group in Fig. 26 may be regarded as representing the middle and top layer of one of the "mulberries" of Fig. 23. You can imagine a bottom layer to exist, and if its units

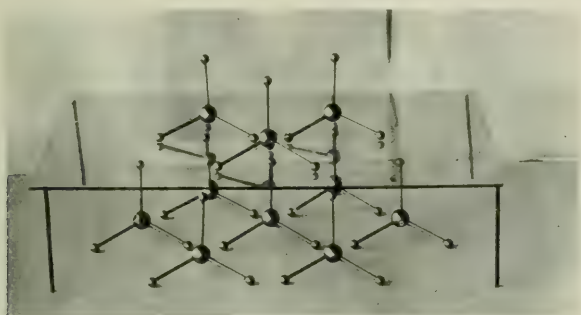


FIG. 26.

are not in the position *vis-à-vis* to the units of the top layer, but in the alternative position, we have an assemblage possessing cubic symmetry.

Now return for a moment to the model with balls. I want you to think of what happens when twinning occurs. Twinning will occur on this plane if the top layer be turned round through 180° ; and that means that the balls occupy the alternative hollows in the layer of balls below them.

Here (Fig. 27) we have them so grouped in the magnetic, or rather the polar, model. The two layers are now in twin relation with one another. The three units on the top are each turned round through 60° (which is equivalent to a turning of them through 180°), and are shifted into the other set of hollows; and those two movements, the turning and shifting, cause the poles to engage again with the cor

puscles. The interesting point about this particular case is that they are just as stable in the new position as they were before. Therefore this model, to my mind, has the serious objection that it makes twinning far too easy. It appears to be an even chance in this case when any layer is deposited whether it is deposited in the regular cubic form or in the twin form.

A few words of explanation may be required here to prevent a possible misunderstanding. In speaking of Fig. 23 I said that if we turned the top layer round through 180° , as in the right-hand figure, we passed from cubic to hexagonal piling. Now, you observe, I also say that the turning of

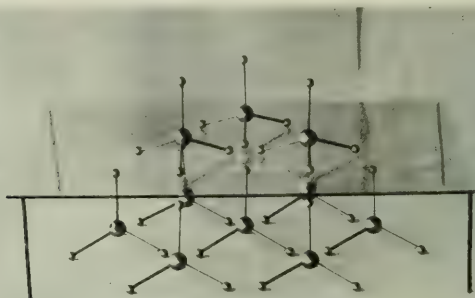


FIG. 27.

the top layer round means the beginning of the formation of a twin. To reconcile these two statements, you must think of what happens when we go on to place other layers above the three. If in placing a fourth, fifth, sixth layer, and so on, we follow the same rule as in the right-hand mulberry of Fig. 23, putting the balls in each layer *vis-à-vis* with those in the layer next but one below, we get a hexagonal crystal. If, on the other hand, the change from regular cubic piling occurs at one plane only, and after the changed layer has been laid down the succeeding layers are piled cubically with respect to it, we have a twin structure in which the plane at which the change occurs is a junction plane connecting two portions which are in twin relation to one another, each of which possesses the symmetry of the cubic system. It may

help to make the point clearer if I add that we may regard hexagonal piling as equivalent to cubic piling with twinning on every layer.

Pass now to this other model (Fig. 28), where each structural unit has six poles, situated at the ends of three rectangular axes, or, in other words, at the six corners of a regular octahedron. Imagine as before that the poles are all of the same sign in all the units, and that there are corpuscles of opposite sign in the interstices between the units—one corpuscle per unit. The units group themselves in closest-packed cubic order as in the figure, each corpuscle engaging six poles, which form an octahedral cluster around it. There is only one corpuscle

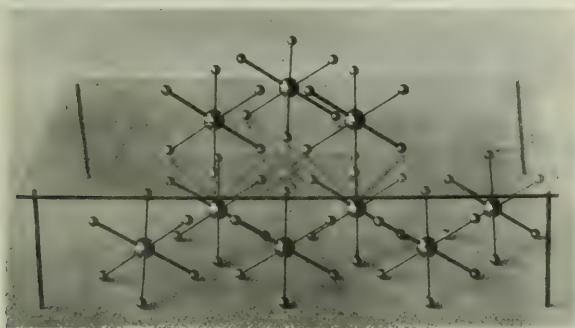


FIG. 28.

required per structural unit. If we attempt to change the upper layer into the position for twinning, by turning the units in that layer through 180° , and shifting them over to the unoccupied hollows of the layer below, we shall find that we leave three balls unengaged. The "cementing corpuscle" then engages with only three poles at the twin surface, leaving three poles with their affinity for a corpuscle unsatisfied, and therefore I should say that with this six-pole model twinning is unlikely to occur.

Finally, consider a model in which each unit has eight poles situated at the corners of a cube (Fig. 29). In this case the central boss is shaped as a cube, instead of a ball, simply for convenience of construction. Fig. 29 shows a single layer of such units; Fig. 30 shows two layers, the upper layer con-

sisting of three units. They are in closest-packed cubic grouping. To hold them in this position requires two corpuscles per

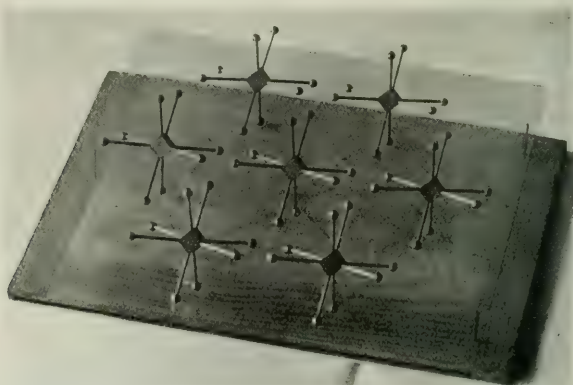


FIG. 29.

unit instead of one, and, as before, you are to imagine the corpuscles to be present though they are omitted in the

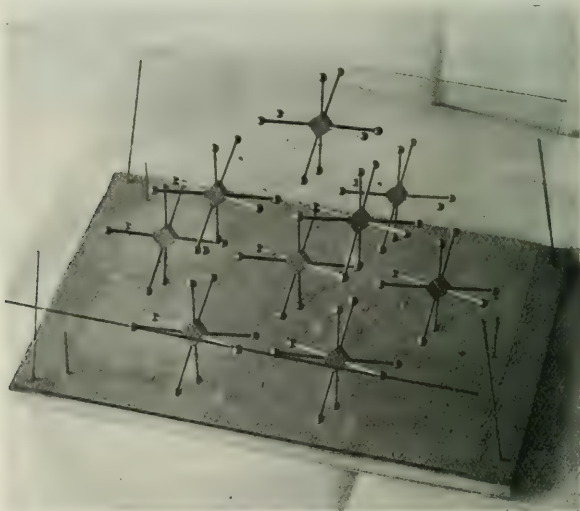


FIG. 30.

model. Each corpuscle engages with four poles, which form a tetrahedral cluster around it. If we attempt to pass

PLATE I

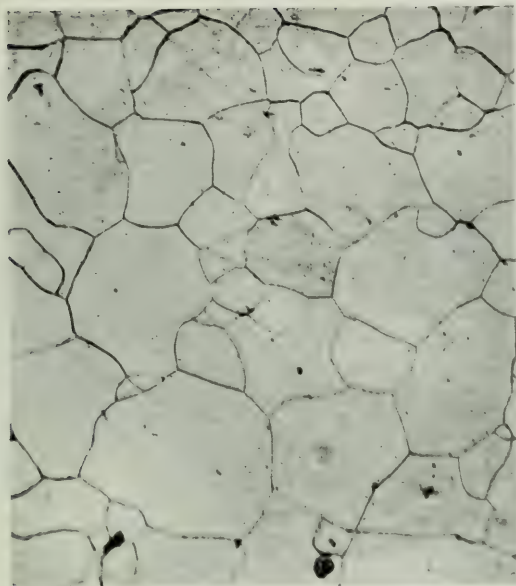


FIG. 1.—Bar Swedish Iron as Rolled.
Magnified 150 diameters.

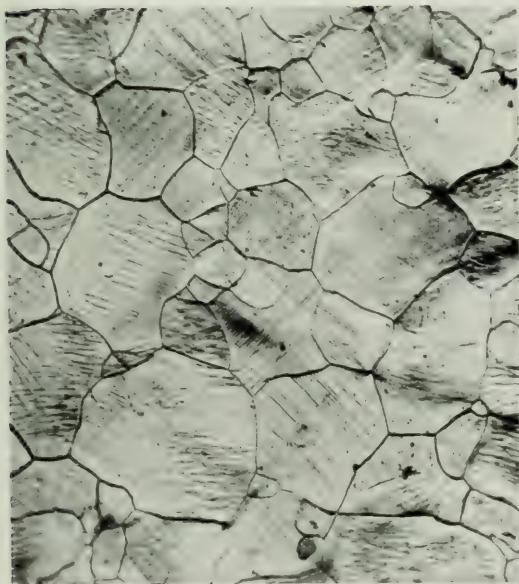


FIG. 10.—Same surface as Fig. 1 after straining in
tension, showing slip bands.

PLATE II

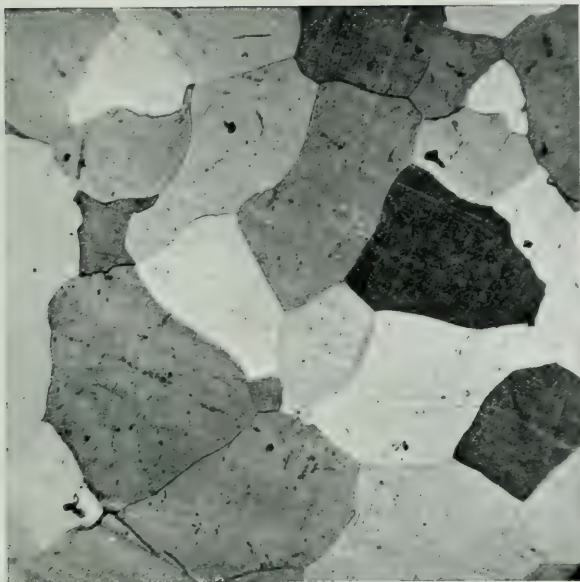


FIG. 2.—Nearly pure iron annealed in hydrogen and deeply etched. Magnified 100 diameters. Vertical illumination, (Rosenhain.)

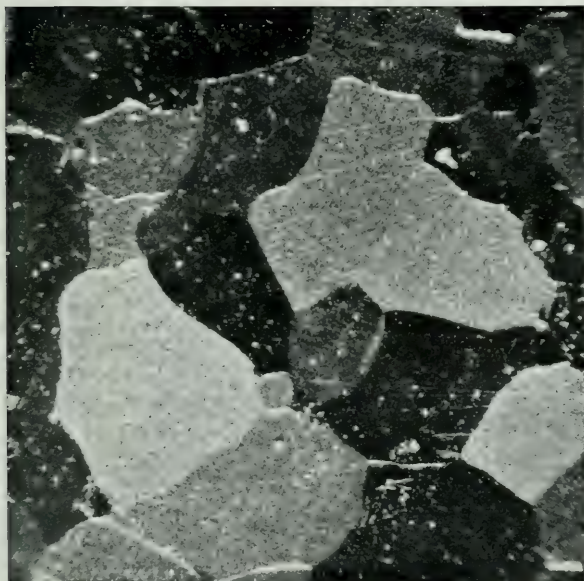


FIG. 3.—Same surface as Fig. 2, but with oblique illumination.

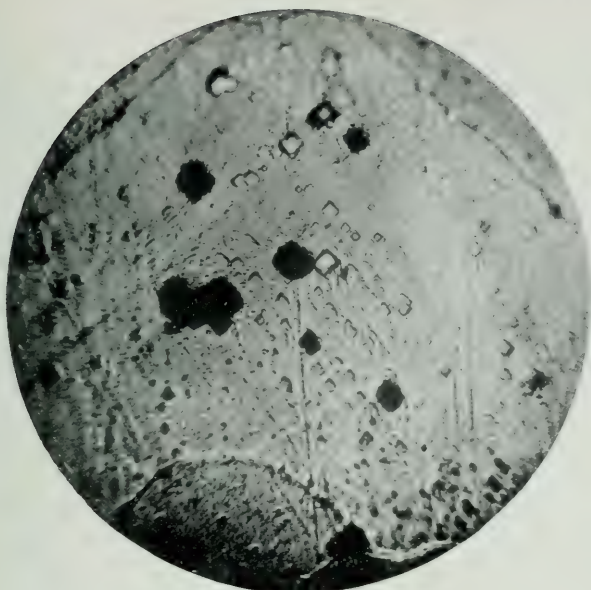


FIG. 4.—Iron, showing pits produced by etching.
Magnified 800 diameters.

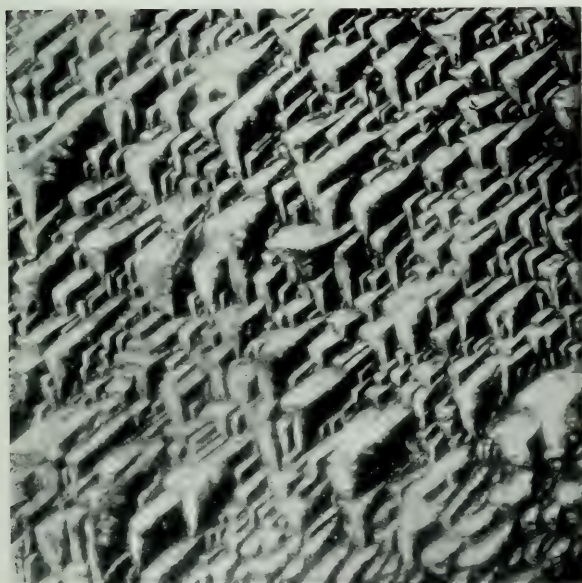


FIG. 5.—Silicon Steel. Magnified 130 diameters. (J. E. Stead.)

PLATE IV

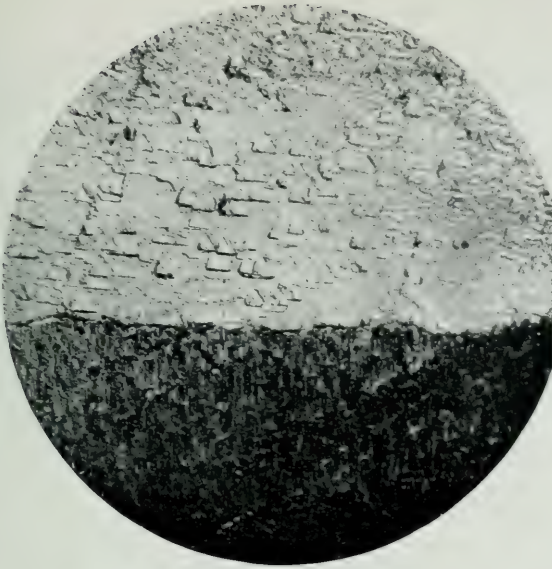


FIG. 6.—Tin plate, showing the boundary between two grains of the tin. Magnified 100 diameters

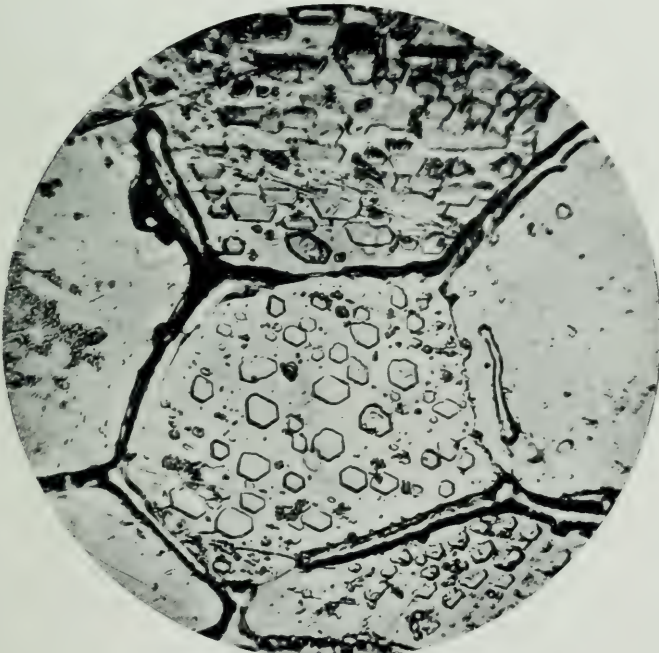


FIG. 7.—Cadmium, cast on a smooth surface of glass (not etched). Magnified 1000 diameters.

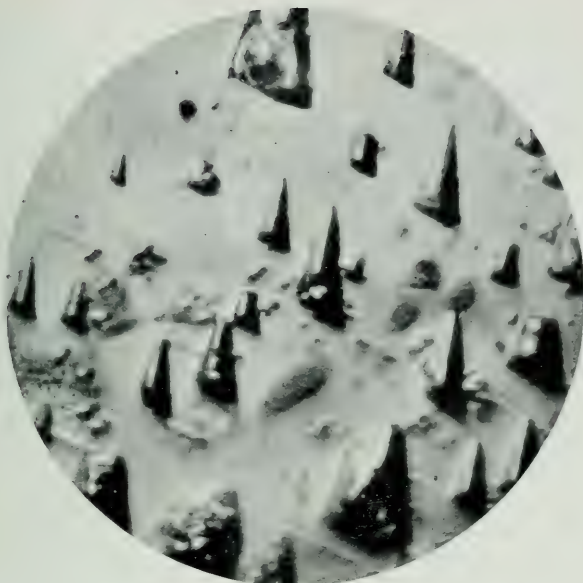


FIG. 8.—Cadmium, cast on a smooth surface of glass (not etched). Magnified 4200 diameters.

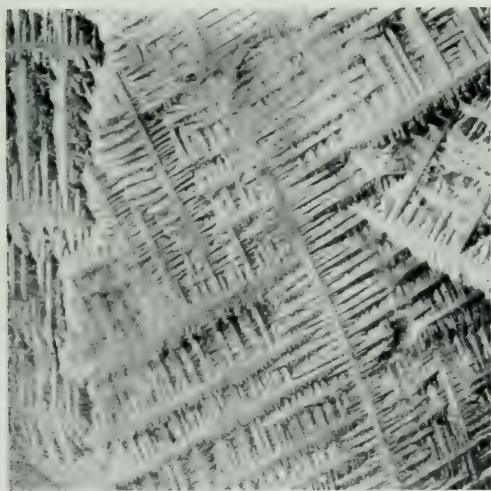


FIG. 9.—Surface of a cast block of antimony, natural size.

PLATE VI

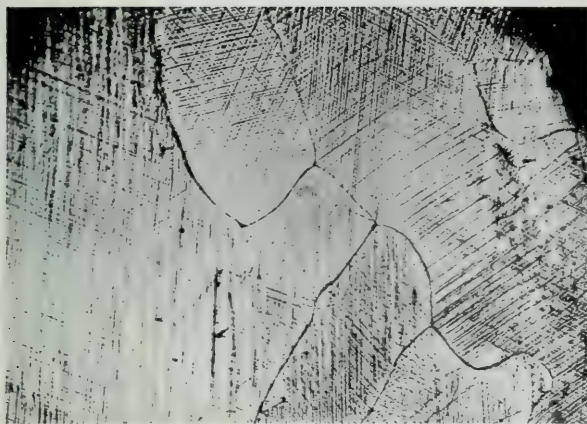


FIG. 11.—Lead after straining, showing slip bands.
Magnified about 60 diameters.

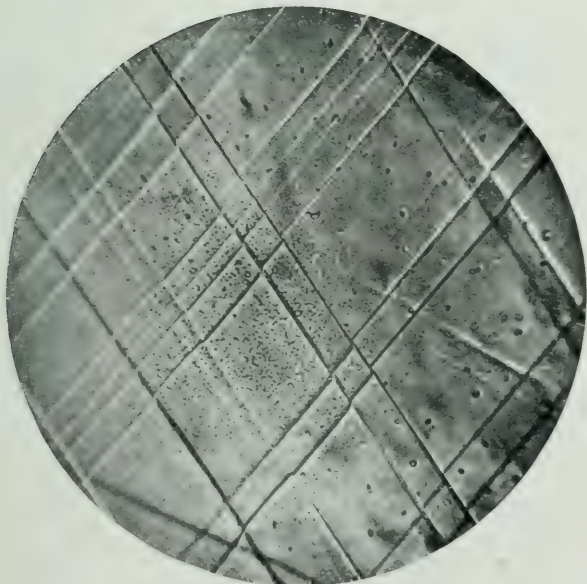


FIG. 15.—Slip bands in strained lead.
Magnified 1000 diameters.



PLATE VII

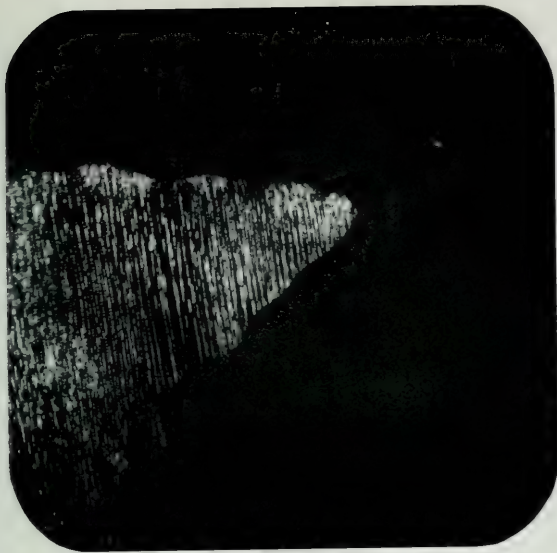


FIG. 13.—Lead after straining, with slip bands shown by oblique lighting. Magnified 100 diameters.

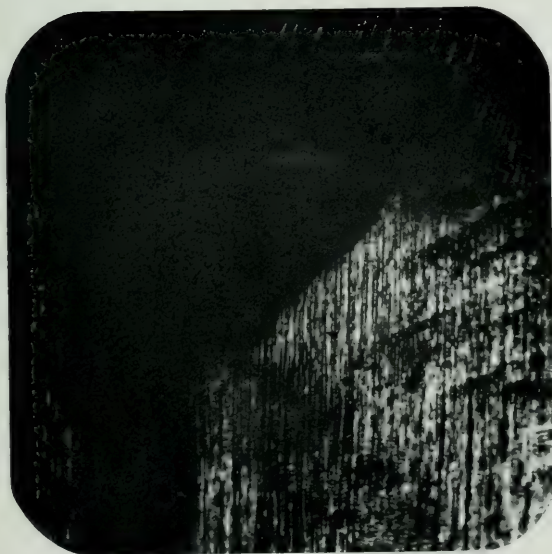
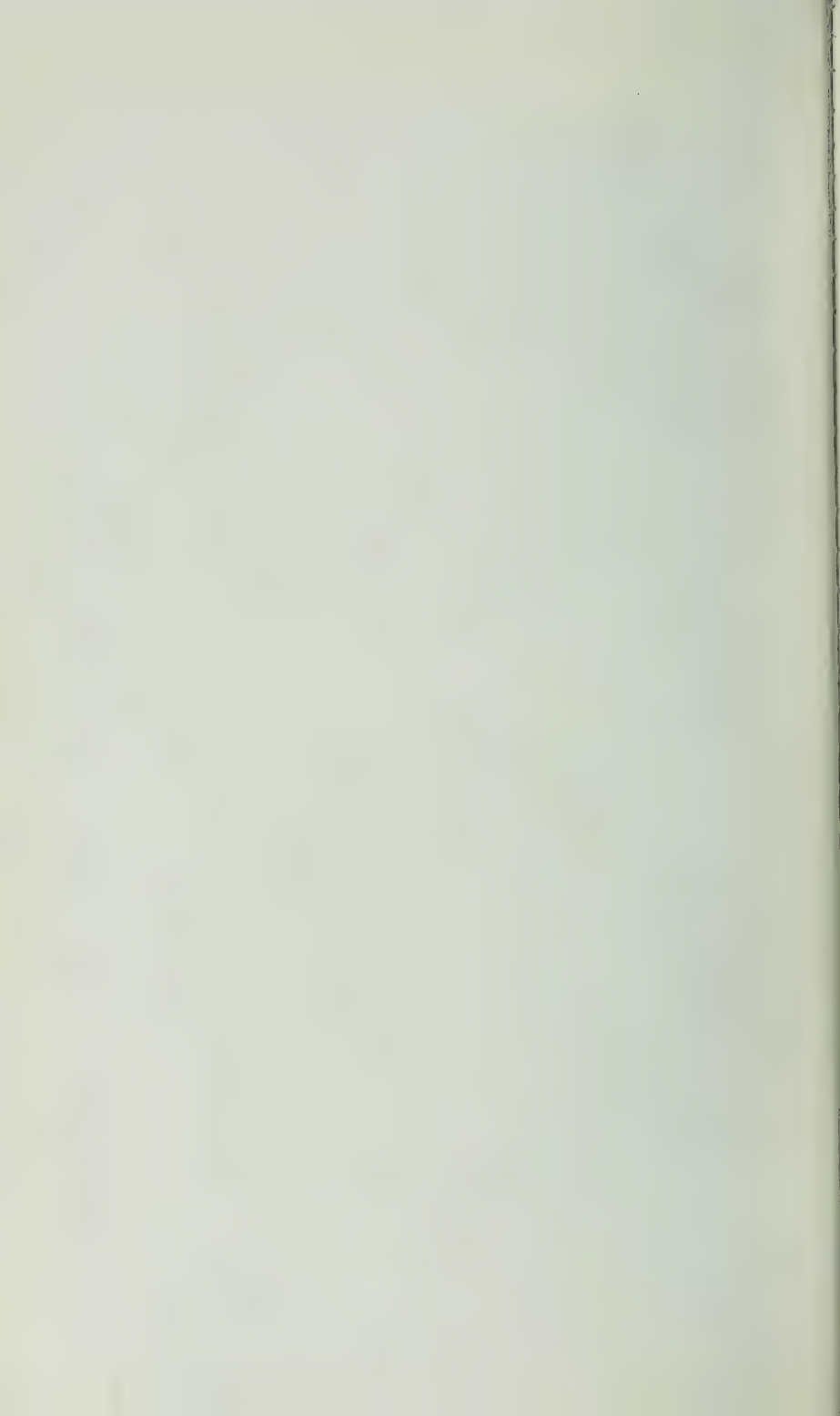


FIG. 14.—Same surface as Fig. 13, but with direction of lighting altered to show slip bands on a neighbouring grain.



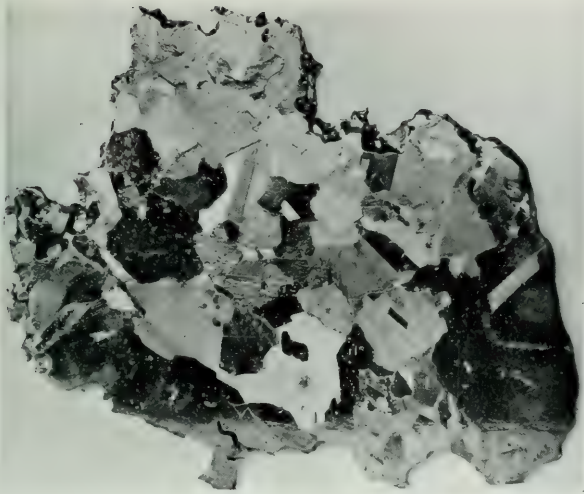


FIG. 16.—Section of Gold Nugget, West Australia,
Magnified $1\frac{1}{3}$ diameters. (Liversidge.)

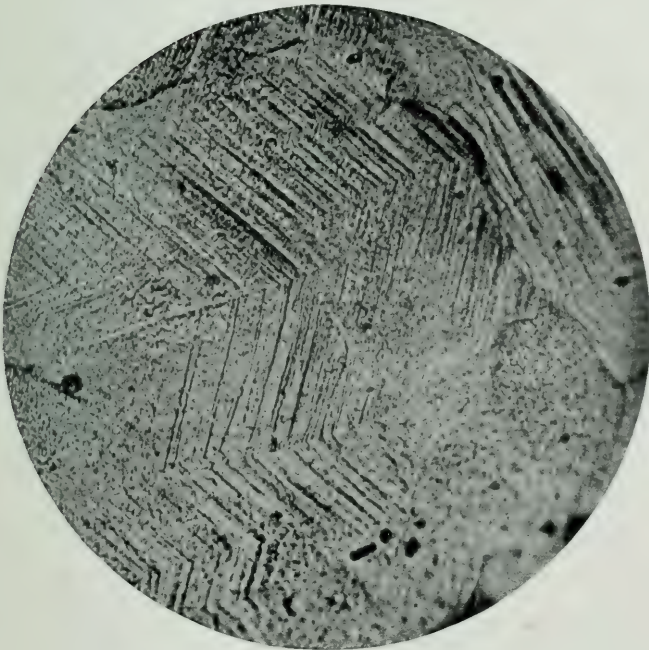
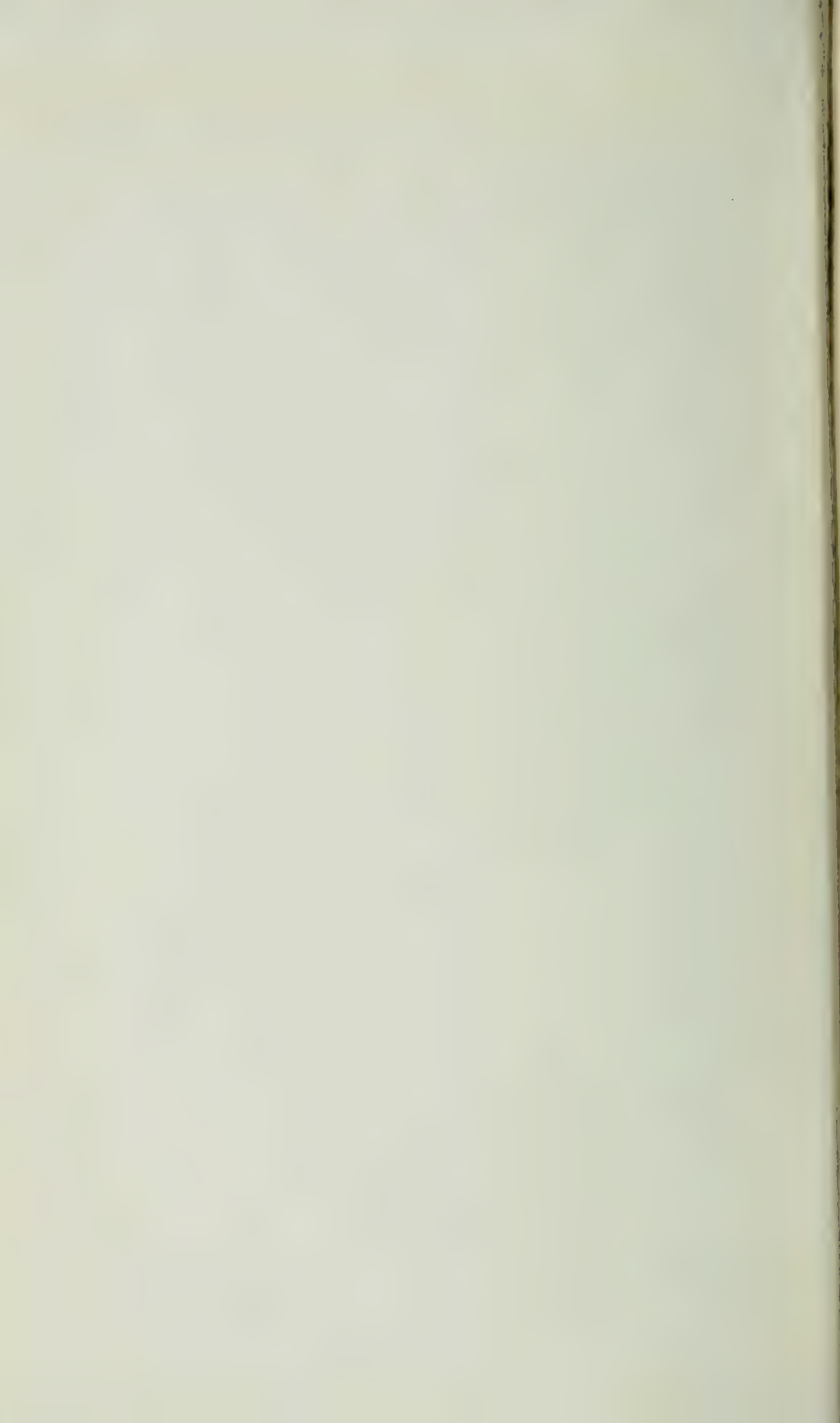


FIG. 17.—Copper, showing slip bands in a twinned crystal.
Magnified 1000 diameters.



to the twin formation by turning and shifting the units of one layer as before, we get that formation with three balls satisfying their affinity for the corpusele and only one disengaged. Consequently we have here what seems to me an exceedingly possible form so far as twinning is concerned, inasmuch as the twin formation, although less likely to occur, is not very much less likely. The stability is not so very different in the two cases.

Fig. 31 shows the same group as Fig. 30, but with the three units which constitute the upper layer turned and

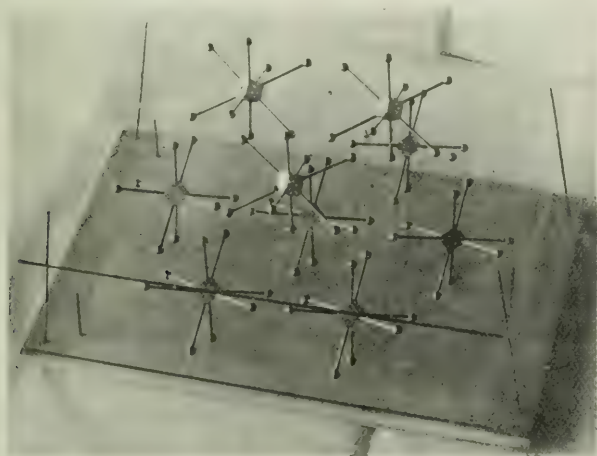


FIG. 31.

shifted into the twin position. It is to be feared that these models are scarcely comprehensible when displayed in photographic pictures. They should be seen at close quarters, with two eyes, and the units should be handled, to have their grouping properly appreciated.

Some one may be inclined to ask, how can you imagine hexagonal formation to occur? We may, as I have said, regard hexagonal formation as cubic formation with twinning on every layer (perpendicular to the axis of hexagonal symmetry). But that does not help us if we wish to conceive of a polarity in the structural units which will compel them to adopt hexagonal piling. One may obtain that by taking a

model in which each unit has five poles, two at opposite ends of an axis and the other three ranged round the equatorial plane at angles of 120° apart. With such units as these, and with one "cementing corpuscle" per unit, you can build up of necessity nothing else than the hexagonal closest-piled structure.

These points require more illustration than can be given in the limited time of a lecture and without handling the actual models. I have not been able to do more than indicate the scope of the speculations. They make no claim to form a theory or even part of a theory of the constitution of matter. They are rather an attempt to hint at directions one may pursue in search of a solution to the problem; one might compare them to sign-posts on open moorland seen in a fog. They do not satisfy our intellectual curiosity; I shall think they have served their purpose if they stimulate it. In studying molecular structure, we find ourselves in the case described by the Persian philosopher-poet who frequented the doctors—

"And heard great argument
About it and about, and evermore
Came out at the same door as in I went."

It is a study that disappoints and baffles, but even if one feels there is no achievement, its fascination remains. We may never succeed in removing or penetrating the veil, but we are not likely to abandon the effort. As the caged beast goes on beating against his bars, so man will continue to strain after knowledge which, for all that he can tell, may be for ever out of reach.

[The thanks of the Institute are due to the following for permission to reproduce certain illustrations in the above report of the May Lecture:—The Royal Society, Figs. 4, 7, 8, 11, 12, 15, and 17; The Iron and Steel Institute, Fig. 5; The Chemical Society, Fig. 16; and Macmillan & Co., Fig. 22.—ED.]

A STUDY OF THE PROPERTIES OF ALLOYS AT HIGH TEMPERATURES.

By G. D. BENGOUGH, M.A., D.Sc. (THE UNIVERSITY, LIVERPOOL).

THE following is Dr. Bengough's reply to the discussion of the above paper, which was read at the Annual General Meeting, London, January 17, 1912, and was recorded, together with the discussion, in the *Journal*, No. 1, 1912, vol. vii. pp. 123-190 :—

REPLY.

Dr. BENGOUGH wrote that he was much obliged to Sir Gerard Muntz for his interesting remarks. With regard to the exact composition of the alloys to which the term Muntz metal should be applied he was very glad to have the authoritative pronouncement made by Sir Gerard, and would in future only use the term in the sense indicated ; in the past the name had undoubtedly been used in a wider sense, not only by himself but by other metallurgists as well. He was much interested in the agreement between the results obtained in his laboratory experiments and those obtained by the Muntz Metal Co. after years of practical experience ; it was one of the most important functions of the scientific metallurgist to endeavour to shorten the path of the manufacturer towards improved methods and results, and though in this case the practical men had been first in the field, and it had only been left for science to show, in part, the "reason why," nevertheless the agreement in results obtained by such different methods afforded one more illustration of the numerous points of contact between science and practice.

He was very much interested in the differences between rolled and extruded rods mentioned by Sir Gerard ; there was evidently an opening here for a research of great interest.

He was much obliged to Dr. Rosenhain for the kind remarks with which he introduced his contribution to the discussion. With regard to his objection to the experimental method adopted in so far as it depended on the constancy of friction of the ram, he had one or two explanatory remarks to offer. In the first place the packing of the ram was hemp and not leather cup, as in an ordinary hydraulic machine ; this packing had been made with very great care, and had taken a fortnight to introduce ; it would not be satisfactory probably with really high loads, such as were used with most hydraulic machines, but with the comparatively low loads used in this work it answered very well. With regard to the constancy of friction in the machine, the results obtained were sur-

prisingly good. He had found by careful measurements that the variation between the readings given in any experiment with a bar under test, and in a blank test conducted ten minutes afterwards, would not exceed 5 lb. This gave quite a small figure as the maximum percentage error on most of the tests recorded, especially when it is remembered that for the small loads the bars were directly loaded without the intervention of a ram. The best proof, however, of the adequacy of the experimental method was to be found in the satisfactory agreement between the tests carried out on the machine and those done in the ordinary tensile machine. A glance at the tables given for the various alloys would show that the tests carried out on the author's machine were, if anything, in closer agreement with one another than the tests carried out on the same material in the ordinary machine.

With regard to the effect of oxide on the tests, he was quite prepared to agree with Dr. Rosenhain that this was important. As far as copper was concerned he had, in conjunction with Mr. T. Bamford, M.Sc., already begun a research, using a reducing atmosphere. He hoped to communicate the results to the Institute in due course. With regard to the rate of loading he again agreed with Dr. Rosenhain that this was an important factor, and must be taken into account in designing experiments. Possibly it would be better to adopt a constant rate of loading instead of a constant time under load, as had been done in the present experiments. The drawback to adopting a constant rate of loading with the writer's machine was that it was not possible to load very rapidly, and consequently the total time under load became very great when large loads were concerned. On the other hand, the cost of the experiments became very great if an arrangement for mechanical loading had to be devised.

He was much interested in Dr. Rosenhain's remarks on the nature of the inter-crystalline cement in metals, and the view expressed was an important contribution to the study of the subject. Further experimental work on the matter was urgently needed.

He tendered his best thanks to Professor T. Turner for his contribution to the discussion. With regard to his reference to Fig. 22, he had not intended that diagram to be used in a quantitative manner, but if it were to be so used he agreed with the Professor that it was too wide from Y to C. Professor Turner's explanation of the fact, that in the vast majority of cases it was impossible to do more than double the tensile strength of metals by mechanical work, was a very interesting corollary that followed from the theory that an inter-crystalline cement existed in metals; he was much obliged to Professor Turner for bringing it forward.

Professor Carpenter had asked him whether he regarded the recuperation temperature as an actual point. In reply to that he desired to say that he did not. He regarded it rather as a narrow range over which the two branches of the curve merged gradually into one another. For the sake of precision he had, in the first instance, drawn the diagrams so that the two branches met at a point, but, as he had mentioned at the bottom of p. 143, he believed the two portions of the curve merged gradually.

Professor Carpenter further asked him for an explanation of the curve shown on p. 155. He was obliged to admit that he could not give a satisfactory one. He would prefer not to attempt to do so till he had accumulated further results on alloys consisting of two phases. He was glad that Professor Carpenter had referred to the results obtained by himself and Mr. Edwards on chill cast and rolled copper-aluminium alloys. Although he was familiar with that standard work, the results mentioned by Professor Carpenter had escaped his memory at the time of writing his paper. He had no doubt that Professor Carpenter had supplied the correct explanation of his own results; nevertheless the diagram given by him (Dr. Bengough) applied to the vast majority of other cases met with in practice.

Mr. Boeddicker doubted the accuracy of the analysis given as representing the copper-nickel alloy used in the tests, and deprecated the practice of returning metals by difference. Reference to the table on p. 141 would show that only the copper and the aluminium were so returned, and then only in the cases of these metals themselves, after all the usual impurities had been determined separately. In the case of the copper-nickel alloy all the three constituents had been determined as given in the table, and it was to some extent chance that they had added up exactly to 100 per cent. He had confidence that that result was nearly correct, and had not in consequence sought for the graphite and other constituents mentioned by Mr. Boeddicker. If they were present at all, it would only be in very small proportions. In view of Mr. Boeddicker's interesting remarks on the working properties of copper-nickel alloys, he would further examine some alloys of that series.

Mr. Hudson had suggested that the question of recrystallization had not been sufficiently taken into account in the consideration of the results. It was quite true that in the case of 70/30 brass the temperature of recuperation corresponded approximately with the lowest temperature of really active recrystallization. Another point was that the exact position of the recuperation range appeared to depend on a number of factors that had not yet been sufficiently studied. One of these factors, for instance, was the rate of loading. Others, probably, were the total time in the furnace and the presence of even very small quantities of impurities. He thought that these factors had rather less influence on the temperature of recrystallization; nevertheless there was probably an intimate connection between the two. With regard to the suggestion that fully annealed metal would be better than cast metal as a standard of comparison, it should be remembered that any metal tested in the manner described in the paper received necessarily a fair amount of annealing before it was tested, and he had thought that strains due to casting would largely be removed in that way. Still it was of course possible that some residual strains would be present, and in that case fully annealed metal would be better as a standard. With regard to Mr. Hudson's question as to the "cry" of the metals used, he had noticed in two cases that it had persisted at

temperatures above the recuperation range ; this phenomenon, however, required further investigation.

Mr. Rhead had dealt principally with the theoretical side of the paper. He was prepared to admit that the view put forward by Mr. Rhead was a tenable one, and the only objection to it was that it seemed to be inadequate to explain all the phenomena observed. If one attempted anything like a complete explanation one found oneself driven beyond the position taken up by Mr. Rhead. He (the writer) did not, of course, claim that the theory advanced in the paper was in any way complete or final. He had some experimental work already in hand which he hoped would throw further light on the theoretical side of the subject.

In introducing his paper at the meeting of the Institute in London he had tendered an apology to Professor Huntington for the omission from his paper of a reference to the curves contributed by Professor Huntington to a discussion that took place at the Institute of Mechanical Engineers. As his introductory remarks had not been reproduced in the *Journal*, he took this opportunity of repeating that apology. He trusted that Professor Huntington would carry out his suggestion of bringing together all his work on the properties of metals at high temperatures, and present them to the Institute in the form of a paper. He was much interested in the details of the experiments mentioned by Professor Huntington, and he had evidently investigated the conditions of plasticity at moderate temperatures in greater detail than he (the writer) had done. He thanked Professor Huntington for his concluding remarks.

In reply to Mr. Bannister's written communication, he desired to thank that gentleman for his appreciative remarks and for his suggestions in regard to the method of drawing the curves. With regard to the curve for the elongation of the complex brass in particular, he thought Mr. Bannister's suggestion was valuable.

He agreed with Dr. Desch's remarks on the importance of the time factor in connection with the range of recuperation. He fully intended to carry out further experiments on that matter ; in fact, the work had already been begun. He readily admitted that there were a number of difficulties in the way of the suggestions he had put forward in connection with the transformation of amorphous into crystalline material at high temperatures, especially when Dr. Beilby's work was remembered. He put forward his suggestions as provisional only, pending further work. He was indebted to Dr. Desch for his kind remarks.

With regard to Mr. Sheppard's remarks on the elongation of Muntz metal A, he would suggest that the range of brittleness met with in practice in the case of metals of this type was really the range between 370° and 400° C. In this range he had found that the metal really had a low elongation. It must be borne in mind that the mechanical effect of the transformation point discovered by Carpenter and Edwards had not yet been correlated with mechanical tests ; in fact he (the writer) believed that the only published tests which bore

on the point were his own. Unless Mr Sheppard could say from actual measurements of his own that the point of brittleness corresponded with the Carpenter and Edwards transformation, he preferred to believe that that point had but little mechanical effect, except perhaps after long periods of time and heat-treatment, and that the practical range of brittleness occurred at a lower temperature in the case of ordinary metals of the Muntz-metal type. He was obliged to Mr. Sheppard for his remarks on cast aluminium; he would remark, however, that a study of the back volumes of the Institute's Journal would show that better results than those mentioned by Mr. Sheppard were claimed by some people for pure aluminium castings, and had been obtained by Carpenter and Edwards in their work on the copper-aluminium alloys.

In reply to Mr. Vaughan Hughes he desired to say that he fully appreciated the importance of carrying out tests in a non-oxidizing atmosphere, and experimental work in this connection had already been begun. He had evidence that under such conditions the shapes of the curves were to some extent modified, as had been anticipated by Mr. Hughes. Finally he felt it necessary to say that Mr. Hughes went a little further than he (the writer) was prepared to do in drawing practical deductions as to rolling temperatures from the experimental work now published. It must be remembered that this, after all, was only a preliminary paper, and it was almost certain that further work would bring out additional facts which would necessitate considerable modifications in any practical deductions drawn from the work in its present stage. He was carefully bearing in mind the practical bearings of the work, and he hoped in the future, when he had accumulated a great deal more knowledge, to make some suggestions on the lines indicated by Mr. Hughes.

LONDON MEETING.

THE FIFTH AUTUMN GENERAL MEETING OF THE INSTITUTE OF METALS was held at the Institution of Electrical Engineers, Victoria Embankment, London, W.C., on Wednesday and Thursday, September 25 and 26, 1912, Professor W. GOWLAND, F.R.S., Assoc.R.S.M., President, in the chair.

WELCOME BY THE PRESIDENT.

The PRESIDENT, in opening the meeting, asked to be allowed first of all most heartily to welcome, on behalf of the Council, the London members of the Institute, and himself, the country members and their friends to the Autumn Meeting. The Institute had hoped as usual to have held the Autumn Meeting at one or other of the great centres of metal working in the Provinces, but it had not been possible to make satisfactory arrangements during the present year, so that the Council had been compelled to hold the meeting in London. Unfortunately, London occupied, as regards the great metal working industries, a position of what might be termed secondary importance, so that there were very few works available for the inspection of the members. The Chief Superintendent of Woolwich Arsenal, the Director of the National Physical Laboratory, and the Directors of Messrs. Fraser & Chalmers had, however, very kindly given permission to the members to visit their respective establishments, and he was sure they would find in each of those works more than sufficient of interest to repay their attendance. So far as the position of the Institute was concerned, the members would be pleased to hear that the membership had now reached about 600, which he thought was an extremely gratifying number when it was borne in mind that the Institute was only a little over four years old. During that short lifetime a very large amount of excellent work had been done with regard to the constitution, properties, and the practical working of metals. That it had met with the special appreciation

of workers in the non-ferrous metals who were not yet members of the Institute, but who he hoped would soon join, and that the Institute was working along the right lines, was well shown by the sale of the *Journal*, which during the past year had reached the very respectable sum of £160. That, he thought, was an excellent testimony in favour of the work that had been done, and that the Institute was doing. The work of the Corrosion Committee was proceeding very satisfactorily, but as the members well knew experimental work in which time was a factor could not be too hastily carried out. The Council confidently expected, however, that a further Report from the Corrosion Committee would be placed before the next meeting of the Institute.

The Minutes of the General Meeting held in London on May 10, 1912, were read and confirmed, and signed by the Chairman.

COUNCIL FOR 1913.

The SECRETARY (Mr. G. Shaw Scott, M.Sc.) read a list of members nominated by the Council, and to be balloted for in connection with the election of the Council for 1913, which list was as follows:—

President.

* Professor A. K. HUNTINGTON, Assoc.R.S.M.

Vice-Presidents.

(Two to be Elected.)

† W. H. JOHNSON, B.Sc.	Manchester.
* Professor T. TURNER, M.Sc.	Birmingham.

Members of Council.

(Eight to be Elected.)

† Professor A. BARR, D.Sc.	Glasgow.
† T. A. BAYLISS	Birmingham.
† G. T. BEILBY, LL.D., F.R.S.	Glasgow.
* CLIVE COOKSON	Newcastle-on-Tyne.
* ARNOLD PHILIP, B.Sc., Assoc.R.S.M.	Portsmouth.
* Sir WILLIAM E. SMITH, C.B.	London.
* LEONARD SUMNER, M.Sc.	Manchester.
† CECIL H. WILSON	Sheffield.

* = New Nomination.

† = Retires. Eligible for re-election.

The PRESIDENT stated that the result of the ballot would be declared at the Annual General Meeting, to be held in London on March 11 and 12, 1913. The President also reminded the meeting that, in accordance with the Articles, Section iii. 16, any ten members might also, at the present meeting, nominate a candidate other than one of those nominated by the Council, but none of the members present exercised their right in this matter.

The PRESIDENT said that, with regard to his own position on the Council, he was unfortunately unable, on the advice of his doctors, to continue the work of the Presidency for another year. He had been working somewhat hard for many years, and he was now urgently advised to work less arduously than he had hitherto done. It gave him very great pleasure to find that his friend, Professor Huntington, had been nominated as President, because as all the members knew he had always had the interests of the Institute at heart, and he was sure he would make a most able President. Although personally he would be no longer President after the current year, he assured the members it would always be his earnest endeavour to do everything he possibly could to promote the welfare of the Institute, and to further its interests. He was extremely sorry to have to report the resignation of Mr. Milton, because that gentleman had always been a most valuable Member of Council. He found, however, that his work at Lloyd's interfered so much with his attendance at the Council Meetings that he was compelled to resign, and the Council had nominated Sir William Smith, who had just retired from the Admiralty, in his place.

Sir WILLIAM H. WHITE, K.C.B., F.R.S. (Past-President), was sure the meeting would desire to at once record its regret that circumstances of health had compelled the President to make the announcement to which he had just given utterance. The members knew that, from the beginning of the Institute, from the very first meetings held for its organization, Professor Gowland had taken the greatest and most active interest in its affairs. They hoped that

the rest which the doctors had prescribed would restore the President to his full vigour, and enable the Institute long to have the benefit of his help and counsel in the conduct of its affairs. He wished to recall to the memory of those present that at the beginning of the history of the Institute it was tacitly understood that the three main divisions of its membership, the Users, the Makers, and the Scientific Workers, should in succession be represented in the Presidency. It so happened that, much against the wish of the first President, the office had to be held for about two years in order that the organization of the Institute might go on unchecked. His friend, Sir Gerard Muntz, who was the second President, did yeoman service for the Institute, and was good enough for the same reasons to continue to hold office for two years. Then came the term of the Scientific Workers, Sir Gerard Muntz having so worthily represented Makers of non-ferrous metals, while the speaker had represented Users. The members all felt that there was no one on the Scientific side better fitted for the office than Professor Gowland, and his appointment was unanimously welcomed. For reasons which the President had just stated he would be able to hold office for one year. Personally he felt—and he believed the feeling was general—that Scientific Workers ought to be represented continuously in the Presidency for the full term of two years as the Users and the Makers had been. In filling the vacancy, which they all so much regretted, he was sure there would be a feeling of congratulation and satisfaction that Professor Huntington had consented to be nominated for the vacancy caused by the retirement of Professor Gowland. He desired, in conclusion, to remind the meeting that the Rules prescribed an annual election to the Presidency, and a maximum term of office of two years. He was sure he would not be misunderstood when he added that circumstances might well arise in which it would be to the interest of the Institute and for the convenience of the holders of the Presidency that the existing Rule for the election should be interpreted at times in the sense of limiting the term of Presidency to one year. Indeed there need be no feeling of surprise or injustice if anyone elected to the office

should desire, or if in the interests of the Institute it should be thought preferable, that a single year's Presidency should take place. He hoped in making those remarks he had not trespassed too much on the patience of the meeting. As was well known, he was devoted to the welfare of the Institute, and he believed that the statement he had made would tend to facilitate its good working in the time to come.

The PRESIDENT thanked Sir William White for the very kind words he had just spoken with regard to his services to the Institute.

ELECTION OF MEMBERS.

The SECRETARY read the following list of names of candidates who had been elected members of the Institute:—

NAME.	ADDRESS.	QUALIFICATIONS.	PROPOSERS.
Bolton, Edward John	Lightoaks, Oakmoor, N. Staffs.	Director, Thomas Bolton & Sons, Ltd.	Sir G. Muntz, Bt. E. Mapplebeck. J. G. Brockbank.
Bregowsky, Ivan M.	Crane Company, Chicago, Ill., U.S.A.	Metallurgist, Chief Chemist, Crane Company	W. M. Corse. W. H. Bassett. G. H. Clamer.
Burner, Alfred	Culver Street Engineering Works, Colchester	Managing Director, A. G. Mumford, Ltd.	Sir H. J. Oram. G. G. Goodwin. H. R. Teed.
Garrett-Smith, Noel	Edison & Swan, U.E.L. Co., Ltd., Ponder's End	Chemist to Edison & Swan U.E.L. Co., Ltd.	C. O. Bannister. H. J. Humphries. E. F. Law.
Graham, Alfred Henry Irvine	Fuller's Cottage, Ditton Road, Surbiton	Engineer to Thermit Limited	R. Stutz. W. R. Barclay. J. T. Milton.
Guess, George A.	Oakville, Ontario, Canada	Professor of Metallurgy, University of Toronto	A. Stansfield. W. A. Carlyle. W. H. Merrett.
Holt, Thomas William	103 Wakefield Road, Stalybridge	Manager, Sidney Moorhouse & Co., Ltd.	B. S. Harlow. A. Carter. T. G. Wainwright.
Hull, Daniel Raymond	American Brass Co., Kenosha, Wis., U.S.A.	Metallurgist to American Brass Co.	W. H. Bassett. W. M. Corse. J. A. Capp.
Johnson, Albert William (Student)	31 Angus Street, New Cross, S.E.	Assistant Manager, Metal Warehouse	A. M. Bowes. H. R. Brain. C. W. Wright.
Malby, Seth Grant	Malby & Lucey, Ogdensburg, N.Y., U.S.A.	Mechanical Engineer. Engaged in the aluminium business	W. Gowland. G. A. Boeddicker. T. A. Bayliss.
Mills, Harry	Grice, Grice & Son, Ltd., Nile Street, Birmingham	Copper and Brass Tube Manufacturer	G. A. Boeddicker. C. R. H. Wigginn. A. H. Wigginn.
Palmer, Arthur Cecil Hunter	410 Strand, W.C.	Civil Engineer	Sir G. Muntz, Bt. G. A. Boeddicker. E. F. Law.

NAME.	ADDRESS.	QUALIFICATIONS.	PROPOSERS.
Price, William B., Ph.B.	Scovill Manufacturing Co., Waterbury, Conn., U.S.A.	Chief Chemist	W. H. Bassett. W. H. Buell. W. Gowland.
Rose, Thomas Kirke, D.Sc.	Ashdown, Northwood, Middlesex	Chemist and Assayer of Royal Mint	W. Gowland. H. C. H. Carpenter. G. D. Bengough.
Sharples, James	846 Ashton Old Road, Openshaw, Manchester	Metallurgical Research Chemist to Beyer Peacock & Co.	E. L. Rhead. H. C. H. Carpenter. J. H. Andrew.
Stalman, Otto	Salt Lake City, U.S.A.	Metallurgical Engineer	M. Ruthenburg. F. W. Harbord. B. Blount.
Thompson, John Fairfield, B.Sc., Ph.D.	Orford Copper Co., Bayonne, N.J., U.S.A.	Chief, Testing Department Orford Copper Co.; Superintendent, Monel Metal Manufacturing Co., Bayonne	J. A. Capp. W. M. Corse. G. H. Clamer.

READING OF PAPERS.

Papers were then read by the following: Professor H. C. H. Carpenter, M.A., Ph.D., Vice-President (two Papers), (Manchester); Dr. T. K. Rose (London); Professor A. K. Huntington, Assoc.R.S.M., President-Designate (London); Dr. W. Rosenhain, B.A., Member of Council, and D. Ewen, M.Sc. (both of Teddington); and Dr. G. T. Beilby, F.R.S., Member of Council (Glasgow). Each paper, with the exception of the latter, was followed by a discussion, a hearty vote of thanks being accorded in each case, on the motion of the President, to the respective authors. The meeting adjourned at 1 P.M. until 10 o'clock on Thursday morning, September 26, 1912.

SECOND DAY'S PROCEEDINGS.

THURSDAY, *September 26, 1912.*

The Second Session of the General Meeting was held at the Institution of Electrical Engineers, Victoria Embankment, London, W.C., on the morning of Thursday, September 26, Professor W. Gowland, Assoc.R.S.M., F.R.S., President, again occupying the chair.

READING OF PAPERS.

Papers were read by the following: Mr. F. Johnson, M.Sc. (Birmingham); Mr. E. F. Law, Assoc.R.S.M. (London); Professor T. Turner, M.Sc. (Birmingham); Mr. A. E. Tucker, F.I.C. (Birmingham); and Dr. F. Carnevali (Turin). Each paper was followed by a discussion (the papers by the two latter gentlemen being discussed jointly), a hearty vote of thanks being recorded in each case, on the motion of the President, to the respective authors.

CONCLUDING BUSINESS.

The PRESIDENT then said that it was his pleasing duty to move the following resolutions:—

“That the best thanks of the Institute be, and hereby are, tendered to the following gentlemen and firms whose kindness has contributed greatly to the success of the London Meeting of the Institute:—

“(1) The Council of the Institution of Electrical Engineers for their courtesy in permitting the use of their rooms on the occasion of this meeting.

“(2) The Directors of Messrs. Fraser & Chalmers, Limited, Erith, who have granted permission to members of the Institute to visit their works, and for their hospitality.

“(3) The Director of the National Physical Laboratory, Teddington, who has granted permission to members of the Institute to visit the National Physical Laboratory, and for his hospitality.

“(4) The Chief Superintendent, Ordnance Factories, Woolwich, who has granted permission to members of the Institute to visit the Royal Arsenal.

“(5) The officials of the Brooklands Automobile Racing Club for their courtesy in allowing members of the Institute to visit the Motor Track and Aviation Ground.”

Professor T. TURNER, M.Sc. (Honorary Treasurer), in seconding the votes of thanks, said he was sure all those who had come up to London for the meeting felt that very admirable arrangements had been made for their reception. The building in which the meetings had been held, both

from its position and from the beauty and convenience of its arrangements, had proved most suitable for the purpose. The members were also much indebted to the authorities of the National Physical Laboratory; and he was very sorry that on the previous afternoon thanks were not expressed to Dr. Rosenhain for the arrangements he had made. He did not feel it was exactly his business to do so at the time, and other people were equally retiring; but he was sure the members desired to express their great indebtedness to Dr. Rosenhain for the arrangements he made and their appreciation of all they saw. Messrs. Fraser & Chalmers were old friends of many of the members, and they were again indebted to them for throwing open their works for inspection; and thanks were also due to the Superintendent of Woolwich Arsenal and the officials of the Brooklands Automobile Racing Club. The excursions had made the visit both instructive and pleasant, and he felt sure the members would very heartily join in rendering thanks to those to whom they were so much indebted.

The votes of thanks were then put and carried with acclamation.

Dr. C. H. DESCH (Glasgow) said he had been asked to undertake the pleasing duty of proposing a very hearty vote of thanks to the President for his conduct in the chair. Professor Gowland was an ideal President of the Institute, seeing that he was a man of the highest scientific distinction, who at the same time had had great practical experience of metals; who could work with small quantities in a laboratory and who was equally at home in the handling of 50-ton lots. No better qualification than that could be imagined for a President of the Institute. As the members well know, the President's range of knowledge of metallurgy was extraordinarily wide. At the present meeting he had drawn illustrations from the Romans and the Japanese, and he might have gone even further back in history, since the present knowledge of the metallurgy of prehistoric times was due almost entirely to the researches of Professor Gowland. He also wished, on behalf of those who had read papers and who had joined in

the discussions, to refer to the great courtesy the President had always shown in the control of the debates, and he therefore had very much pleasure in moving a hearty vote of thanks to him.

Mr. LEONARD ARCHBUTT (Member of Council) said he had very much pleasure in seconding the resolution. He thought the members were particularly indebted to the President for exerting himself so much as he had done, knowing as they did that his health was not very robust at the present time. That was the unfortunate reason of his resigning the position of Presidency at the end of the year. All of those who were present at the reception on the previous evening must have very greatly appreciated the admirable arrangements that were made by the President and the Reception Committee. All the members spent a most pleasant evening. The idea of holding a reception at the Royal United Service Institution was a most happy one, because it was impossible to go to a more interesting place; the music was excellent, and the success and usefulness of the meeting was enhanced by the presence of the microscopes, which enabled the members to see the specimens that had been referred to in many of the papers. He thought the President was heartily to be congratulated on the success of the meeting generally, and thanks were also due to Mrs. Gowland for the part she played in the reception on the previous evening.

The motion was put by Dr. Desch, and carried by acclamation.

The PRESIDENT thanked Dr. Desch and Mr. Archbutt for the kind words they had said in proposing the vote of thanks, and the members for the way in which they had received it. He felt that he had done nothing extraordinary; in fact he feared in some respects he had hardly done his duty, although he had endeavoured to do it. When he found it was impossible for the Institute to hold a meeting at one or other of the chief centres of metal working in the country, he was afraid the Institute could hardly offer the country members

sufficient inducements to come to London, but he believed that had proved not to be the case. He trusted none of the members would regret their visit, and he sincerely hoped they had enjoyed it. Before the meeting concluded he desired to propose a hearty vote of thanks to the Secretary. Mr. Shaw Scott, who had acted as Local Secretary in connection with the meeting, had worked like the proverbial Trojan, and it was impossible for anyone who did not know the amount of organization that was required for a meeting of that kind to appreciate how much he had done. He had very much pleasure in asking the members to accord a most hearty vote of thanks to Mr. G. Shaw Scott.

Mr. W. H. JOHNSON, B.Sc. (Vice-President), said he had very much pleasure in seconding the resolution. He had had the pleasure of knowing Mr. Shaw Scott certainly as long and probably longer than most of the gentlemen present, and to know him was only to recognize the great ability he possessed, and the intelligent use he made of it. He had by his services rendered much benefit to the Institute; further, he had facilitated the occupation of the Chair by the various Presidents in the best way possible, viz. by relieving them of the arduous labour necessary for the carrying out of the meetings.

The resolution having been carried by acclamation, the meeting terminated.

RECEPTION AND VISITS.

In the evening of September 25, 1912, a Reception was given at the Royal United Service Institution, Whitehall, S.W., by the London Meeting Reception Committee, which committee consisted of the whole of the London Members of Council. The members and guests, to the number of about two hundred, were received by the President, Professor W. Gowland, F.R.S., Assoc.R.S.M., and Mrs. Gowland in the Banqueting Hall of the Institution, a photograph of which forms the frontispiece of the present volume.

Visits took place on both days of the meeting after the morning session. In the afternoon of September 25 one party of members went to Messrs. Fraser & Chalmers' works at Erith, another party visiting the National Physical Laboratory at Teddington. On the following afternoon there were again two parties, one going to the Royal Woolwich Arsenal and the other to the Brooklands Motor Track and Aviation Ground.

THE STRUCTURAL RESOLUTION OF THE PURE COPPER-ZINC β CONSTITUENT INTO $\alpha + \gamma$.*

BY PROFESSOR H. C. H. CARPENTER, M.A., PH.D.
(VICE-PRESIDENT).

IN the discussion on the author's paper entitled "Further Experiments on the Critical Point at 470° C. in Copper-zinc Alloys," † he had occasion to state that he had resolved the structure of the apparent β constituent into $\alpha + \gamma$, without having to employ either α or γ in excess of the eutectoid composition. It is quite evident from Shepherd's original diagram of the system that a certain amount of supersaturation can exist at this point, since his β area extends from 53.5 to 51 per cent. of copper. The author had hoped to determine its exact position, but, as explained on p. 98, owing to the great brittleness of the γ constituent, which breaks up and falls out during polishing, especially when it exists in large pieces, the requisite measurements could not be made. The mean figures, however, viz. 52.25 per cent. copper and 47.75 per cent. zinc, cannot be far from the actual values, and these will be regarded as the probable figures.

The author, however, is inclined to conclude, from his somewhat extended experience with these alloys, that β is more readily supersaturated with γ than with α . He has never observed the lamellar decomposition of β on the γ side, and the γ always appears to separate abruptly, as from a supersaturated solution, whereas on the α side the lamellar resolution has been several times noticed. Probably, therefore, the eutectoid composition is a little higher in copper than that given above, but how much there is no means of estimating.

While on this point, and in view of the discussion on the author's previous paper, it may not be superfluous to remark that there is no reason why the resolution of a eutectoid

* Read at Autumn General Meeting, London, September 25, 1912.

† *Journal of the Institute of Metals*, No. 1, 1912, vol. vii. p. 90.

should present the same structural appearance on each side of the eutectoid point. On the contrary, the presumption is that the structure will be different, because its exact form will depend on the character of the component in excess.

Guertler* even goes so far as to say, when discussing the copper-tin eutectoid inversion of V. to I. and VII., "Alle Dystektika verändern ihr Aussehen merklich mit dem Wechsel der in Überschuss anwesenden Komponente."†

The position reached in the author's previous research was that a pure apparent β alloy, composed of 52.12 per cent. of copper and 47.86 per cent. of zinc after six weeks' annealing at 445° C. under conditions which prevented any change of composition, showed no signs of α and γ visible at 150 diameters magnification. In some places the apparent β areas were found to have grown; in others, however, signs of the breaking up of the original crystals were evident. In view of the last-named fact, the annealing was continued for a longer period, and the test finally extended to a period of four months, the specimen being examined every fortnight. It was found that the breaking up of the apparent β crystals into much smaller crystals continued. These, however, were manifestly of the β type, although a careful examination of the new crystals revealed the presence of numerous specks, which may perhaps be regarded as evidence of incipient resolution. Whereas the original β alloy showed not more than four to six crystals in any given field, the drastically annealed alloy revealed sometimes as many as fifty. Plate IX. No. 1 shows an area containing about twenty-five, and this may be compared with Plate IV. No. 1 of the author's previous paper for evidence of the presence of the specks referred to above. Four months' annealing, however, did not carry the resolution any further than this. Practically, therefore, the structure of the pure eutectoid $\alpha + \gamma$ alloy may be regarded as absolutely stable. It cannot be upset by any annealing however prolonged, and in this respect it appears to be perfectly unique. This stability is remarkable when it is remembered

* *Metallographie*, p. 670.

† *i.e.* all eutectoids change their appearance markedly when the component in excess changes.

that the presence of quite a small excess either of α or γ is sufficient to bring about the structural resolution into $\alpha + \gamma$.

In his previous paper the author put forward the following view:—"The peculiarly persistent structural stability of the pure eutectoid alloy can be explained by supposing that at the inversion temperature on cooling the resolution $\beta \rightarrow \alpha + \gamma$ takes place throughout the entire alloy almost, if not quite, simultaneously. This constitutes a favourable condition for the production of the inversion products in an amorphous form, because the forces operative in crystal formation do not have time to come into play."

Regarding the alloy from this point of view, it was considered that repeated quenching in liquid air might cause one or both of the constituents to crystallize from the amorphous complex. Two specimens were treated in this way. They were kept for four hours in liquid air, then allowed to warm to the ordinary temperature and again quenched. After six treatments they were microscopically examined. Numerous specks were found in the large β crystals. They were distributed in haphazard fashion; some crystals were quite free from them, others had large numbers. The general effect was one of spontaneous crystallization from a supercooled material. The experiments were continued for another twelve quenchings, when the white spots were found to have grown, and small bluish-grey ones, very like γ , had made their appearance. Finally, the alloys were allowed to stand for a fortnight at the ordinary temperature. After this the decomposition of β appeared to have proceeded to a considerable extent and in various ways:—

(1) The first type is shown in Plate IX. No. 2, consisting of numerous white crystals, chiefly of cubic or octahedral section, but showing in the left-hand corner some of tetrahedral section.

(2) The second type represented in Plate X. No. 3 is of the same general character, but the white crystals are exclusively of the tetrahedral type, and the ground-mass of apparent β shows signs of breaking up.

(3) A third type is seen in Plate X. No. 4. It bears certain resemblances to Nos. 2 and 3, but the large white

crystal shown in the upper part of the field exhibits no crystallographic regularity, such as the preceding types do.

(4) A fourth type, of a quite different character, is shown in Plate XI. No. 5. A number of apparent β crystals were found to have been completely resolved into a granular complex of light and dark crystals, such as is shown in the centre of the field. These specimens were then annealed for ten days at $420^{\circ}\text{C}.$, with the idea of coarsening the structure of the resolution products. After this treatment the granular decomposition was found very much developed in certain parts, stretching like a comet's tail in a matrix of unaltered β . The photograph shown in Plate XI. No. 6 represents a part of one such area, in which the resolution products appear white and black and unaltered β half-tone. The white crystallites of definite crystallographic form were now seen to have disappeared.

The specimens were then subjected to twelve more liquid air quenchings with a view to developing the above structure still further, followed by another annealing. A most surprising result was obtained. Not only had the above development been arrested, but it had to a great extent disappeared and been replaced by apparent β areas. After further experiments of this character it became clear that the above types of structure, Nos. 2-6, do not represent stable resolution products of the apparent β constituent. Exactly what they are it has been impossible to discover, but in any case they appear to be transitory and not permanent, and the conditions of their appearance are also obscure. They do, however, indicate clearly that apparent β , the alloy of eutectoid composition, is not a homogeneous substance.

It then appeared possible that somewhere between $460^{\circ}\text{C}.$ and the ordinary temperature $\alpha + \gamma$ reacted in such a way as to form one stable phase, and that this was the explanation of the failure to obtain a permanent two-phase structure. Such a case does indeed appear to be furnished by the silver-cadmium alloys, whose equilibrium diagram* presents so remarkable a similarity to the modified copper-zinc diagram put forward by the author and Mr. Edwards.

* *Metallographie*, p. 495.

With a view to testing this, a cooling curve of the alloy was taken from 700°C . down to the ordinary temperature. This is shown in Fig. 1, and it will be observed that below 460° , after the curve has reached its normal slope, there is no irregularity whatever, *i.e.* there is no indication of any other

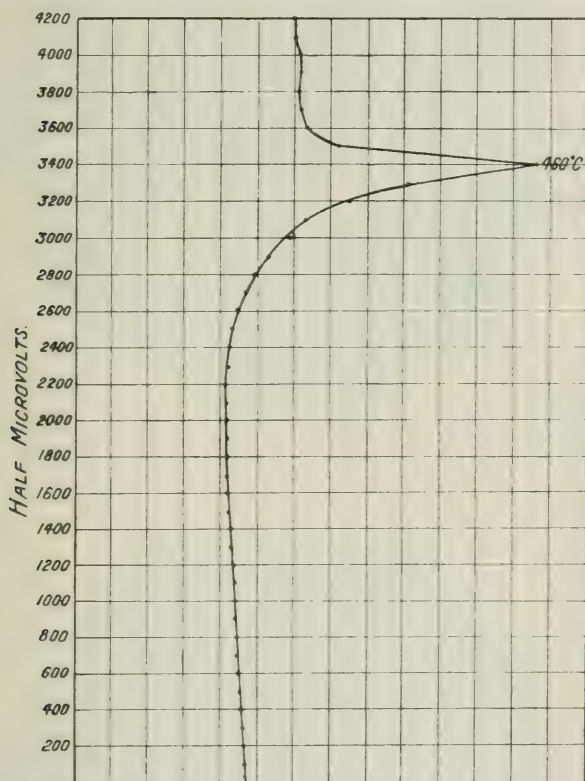


FIG. 1.—Derived Differential Curve.

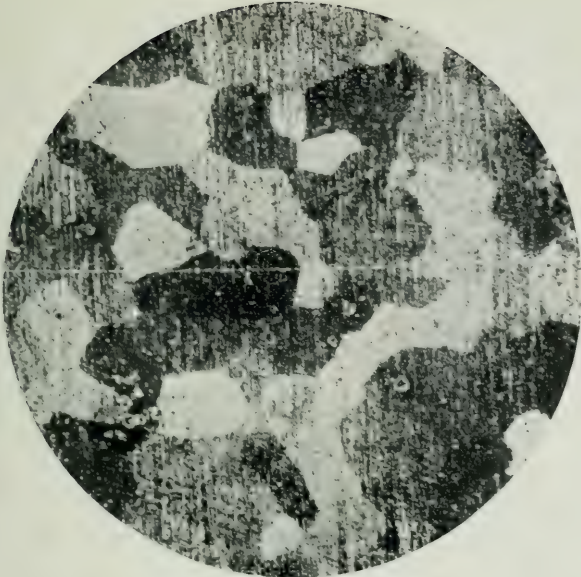
change. The cooling curve therefore gives no support to the view that α and γ react between 460° and the ordinary temperature to form a new phase. It is very difficult to reconcile such a possibility with the results obtained in the author's previous paper,* but it was considered essential to place the matter beyond doubt.

* *Journal of the Institute of Metals*, No. 1, 1912, vol. vii. pp. 70-88.

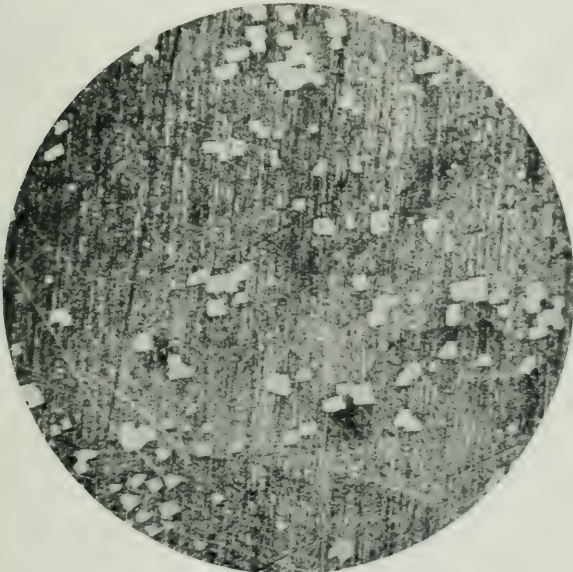
It then appeared as if the solution of the difficulty might be reached by placing the pure apparent β alloy in contact with an alloy of very nearly eutectoid composition which contained coarse α and coarse γ , and annealing them together. Such alloys are furnished in the author's paper presented simultaneously with this on "The Effect of other Metals on the Structure of the β Constituent in Copper-zinc Alloys." And for this purpose the alloy containing 0.95 per cent. of vanadium was chosen (Plate XVI. No. 8 of that paper). This alloy as cast, and without any annealing, shows the complete $\alpha + \gamma$ resolution in a very striking way. The test was carried out as follows:—

The polished and etched vanadium alloy was placed on the polished and etched surface of the pure apparent β alloy. They were sealed up in a glass cylinder in the manner shown in the previous paper, and annealed at 445° C. for five days. On examination it was found that a number of minute specks were visible in the β crystals. The test was continued for nine days, and by this time the colour of the specks, which had grown, was seen to be light bluish-grey. *This is exactly what was to be expected.* The vanadium alloy contained its γ crystals in relief, and the contact between these and the β alloy was therefore more perfect than that of the α crystals. Accordingly they acted as nuclei for the deposition of γ crystallites from the apparent β alloy. Once the action had been started the vanadium alloy was withdrawn, and the annealing of the apparent β continued alone. This extended ultimately over ten weeks, the specimen being examined from time to time. When the test was finished the distribution of the α and γ areas was seen to be very irregular. Two very large areas, occupying a good deal more than the entire field of view of the microscope under low-power examination, consisted wholly of γ . Smaller colonies of γ also occurred here and there. In other parts the field was predominantly α . The colours of these constituents were characteristic, viz. golden-yellow α and light bluish-grey γ . At no stage of the resolution was any lamellar structure noticed, but in view of the notorious transience of this type on heating this need cause no surprise. Plate XII. No. 7 shows a field consisting

PLATE IX

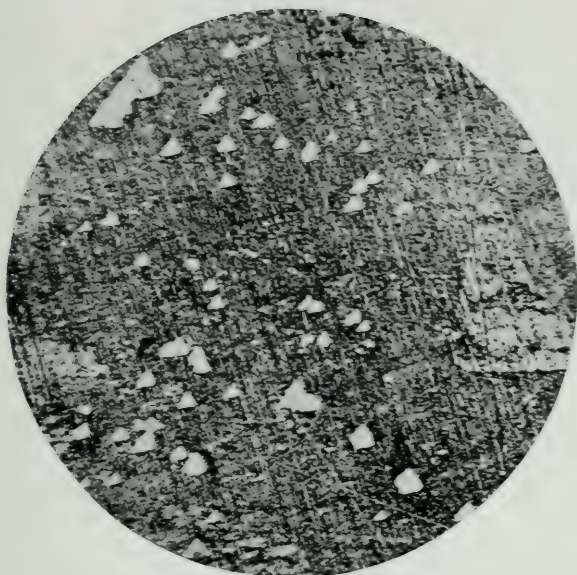


No. 1.—Structure of apparent β alloy after very prolonged annealing at 445° C. The field contains about 25 crystals. Some of these are dotted with specks which may be the first signs of the resolution into $\alpha + \gamma$. Magnified 150 diameters.

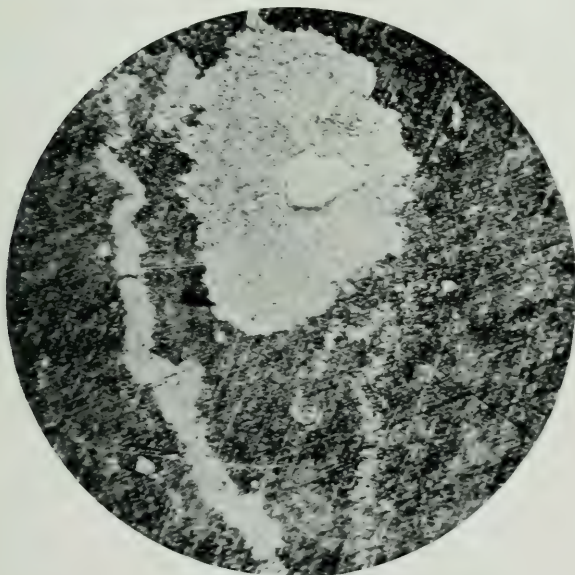


No. 2.—Showing the separation of numerous white crystals, chiefly of cubic or octahedral section, from β caused by repeated quenching in liquid air. Magnified 150 diameters.

PLATE X

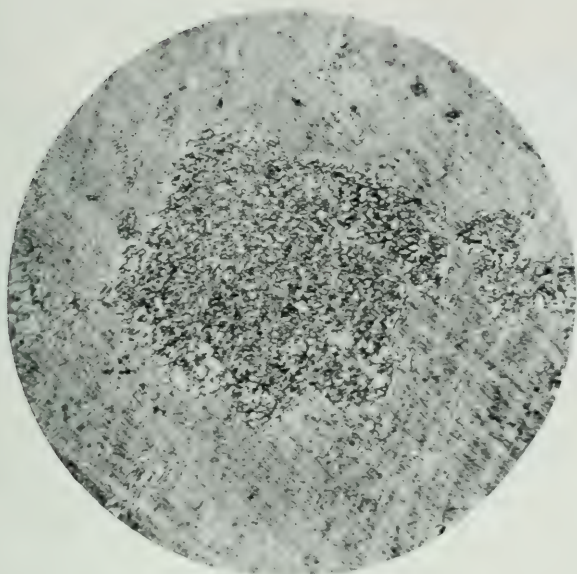


No. 3.—The crystallization is of the same general type as in No. 2, but the sections are those of tetrahedra principally. Magnified 150 diameters.

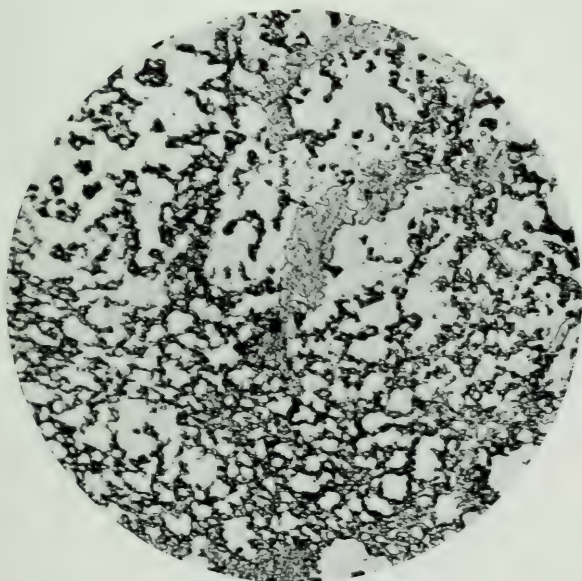


No. 4.—Showing absence of crystallographic regularity. Magnified 150 diameters.

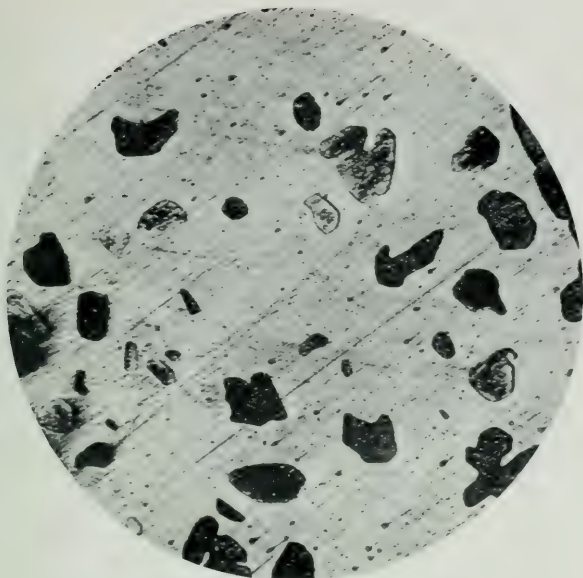
PLATE XI



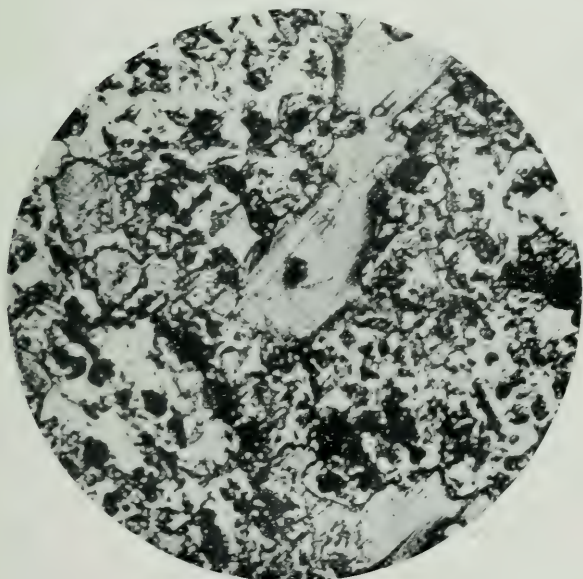
No. 5.—Showing decomposition of central crystal into a granular complex. Magnified 150 diameters.



No. 6.—Showing development of the above after ten days at 420° C.
[White and black areas represent resolution products; the half-tone areas represent unaltered β .] Magnified 150 diameters.



No. 7.—Dark spots, γ ; remainder, α . (Etched specimen.)
Magnified 150 diameters.



No. 8.—The entire field consists of γ , which appears white. The black areas are holes from which the brittle γ has fallen out during polishing. (Specimen polished, but unetched.) Magnified 150 diameters.

chiefly of α , but with a number of γ crystallites, while No. 8 represents an area consisting wholly of γ .

It may be objected that the foregoing does not constitute a decisive proof of the resolution of pure β into $\alpha + \gamma$; that in the test diffusion of γ from the vanadium alloy into the pure β alloy occurred to a sufficient extent to alter the eutectoid composition; that an alloy containing excess of γ was produced, and that this resolved in the same way as the alloy containing excess of γ described in the author's previous paper. The possibility of diffusion has, of course, to be admitted. If, however, it took place from the vanadium alloy into the pure β alloy, it would also take place in the reverse direction. Moreover, the β alloy was, as nearly as can be estimated, of exactly eutectoid composition, and the vanadium alloy was probably not more than 1 per cent. from the same figure. This allows a mean excess of about 0.5 per cent. γ over the two alloys if diffusion occurred. This, however, is insufficient of itself to produce any structurally free γ in an alloy of eutectoid composition, since, according to Shepherd's diagram, a variation of 1.25 per cent. on either side from this still leaves an alloy containing β only. From this it is evident that any changes in composition due to diffusion would not have been sufficient to produce any free γ in the β alloy. It appears therefore to the author that the proof submitted of the resolution of pure apparent β into $\alpha + \gamma$, visible at low magnifications, is free from objections, and is decisive.

When all is said and done, however, the fact remains that in a certain sense the proof is indirect. The outstanding fact, and it is of great significance, is that the so-called β constituent, which apparently possesses a simple structure, although it is indubitably composed of two constituents, viz. α and γ , is structurally indefinitely stable even under conditions which, according to all precedent, should have brought about its decomposition. It must now be admitted that prolonged annealing does not necessarily cause the structural elements of a eutectoid alloy to grow and segregate. Future research must decide whether other alloys of this category exist, or whether the β constituent of the copper-zinc system

is the conspicuous and sole exception to a general rule. In any case, it is the author's conviction that the Muntz metals owe their valuable practical properties to this particular idiosyncrasy of the most tantalizing metallic constituent it has ever been his pleasure to investigate.

SUMMARY.

1. The β structure of the pure $\alpha + \gamma$ eutectoid alloy may be regarded as absolutely stable. It cannot be upset by any annealing, however prolonged, and in this respect it appears quite unique.

2. Repeated quenchings of this alloy in liquid air undoubtedly produce structures characteristic of a two-phase system. These structures, however, are of a transitory nature, and the conditions of their appearance are also obscure. They do not appear to correspond to a segregation of $\alpha + \gamma$ in a coarse crystalline form.

3. Between 460° C. and the ordinary temperature the alloy was found to undergo no other inversion detectible on a cooling curve.

4. Ultimately the resolution of the pure β structure into $\alpha + \gamma$ was brought about by the "nucleus" action of a eutectoid alloy containing 0.95 per cent. of vanadium, which contains its $\alpha + \gamma$ in a coarse crystalline form immediately after being cast. By infecting the pure apparent β alloy with this substance for a short period at 420° C., followed by a prolonged annealing, coarse segregations of α and γ were obtained.

5. A lamellar resolution of pure β was never observed.

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THE EFFECT OF OTHER METALS ON THE STRUCTURE OF THE β CONSTITUENT IN COPPER-ZINC ALLOYS.*

BY PROFESSOR H. C. H. CARPENTER, M.A., PH.D.
(VICE-PRESIDENT).

IN a previous paper† the author has shown that the so-called β constituent in copper-zinc alloys is to be regarded below 470° C., from the standpoint of constitution, as an extremely minute and uniform complex of α and γ particles. From the structural standpoint, however, it may be regarded as a single constituent, because these particles, which are on the limit of microscopic vision, show no signs of coalescence even after six weeks' annealing at 445° C., and thus exhibit remarkable stability. To express this idea the author has suggested the term "apparent β " for the eutectoid alloys, containing, as nearly as can be ascertained, about 52 per cent. of copper and 48 per cent. of zinc. This "apparent β " appears as large irregularly shaped polyhedra of a pronounced reddish-yellow colour.

The experiments described in the previous paper were designedly made with materials of the utmost attainable purity, the alloys containing only four parts of impurities per 10,000. The industrial alloys of copper and zinc, however, do not reach this degree of purity, and some of them contain substantial amounts of other metals, such as lead and iron, often introduced for a specific purpose. It appeared, therefore, important to investigate the effect of such metals on the structural stability of the apparent β constituent.

The added metal may operate in one of the following ways:—

1. It may be quite or almost insoluble in apparent β , and yet, in virtue of a great power of crystallization, it may exert an important influence on the mode of separation of the $\alpha + \gamma$

* Read at Autumn General Meeting, London, September 25, 1912.

† *Journal of the Institute of Metals*, No. 1, 1912, vol. vii. pp. 70-88.

complex at 470°C. ; *e.g.* it may cause these to appear as coarse crystals, and with these would be associated a considerable degree of brittleness.

2. It may possess a limited solubility, and in such a case one of three consequences may follow:—

- (a) It may displace the eutectoid point without appreciably altering the temperature of the inversion. It would probably shift this towards the γ side, and this would have the effect of upsetting the structural stability of the minute $\alpha + \gamma$ complex, and producing brittleness.
- (b) It may not only displace the eutectoid point, but it may also either raise or
- (c) Lower the temperature of the inversion to a definite but not very great extent.

3. It may, if very soluble, lower the temperature of the inversion *below the ordinary temperature*, in which case β would be the stable phase down to the ordinary temperature, and the $\alpha + \gamma$ inversion would thus be completely prevented.

From the practical standpoint this would be a most valuable result, since the alloy would show no tendency to develop brittleness due to the $\alpha + \gamma$ inversion.

The metals may thus be grouped under three main heads:—

- 1. Those which are quite insoluble in copper and zinc.
- 2. Those which are partially soluble.
- 3. Those which are very soluble.

The word soluble is used in the following sections in a somewhat restricted sense. For practical purposes, apparent β will be regarded as one constituent, and any metal which can be assimilated by this without causing a coarse crystallization of the $\alpha + \gamma$ complex or the separation of a special constituent from the apparent β crystals will be termed to that extent soluble.

CLASS I.—METALS OF COMPLETE INSOLUBILITY.

1. *Bismuth.*

The first metal examined was bismuth. This metal is quite insoluble in copper and zinc in the solid state, and it was

thought desirable to investigate its action at the outset, because it is the simplest case from a theoretical standpoint. There are no disturbing effects, owing to the formation of binary compounds. The only outstanding question was, "Would bismuth, with its pronounced tendency to form large well-developed crystals on solidification, cause a separation of coarse $\alpha + \gamma$ from apparent β , and, if not, how much bismuth could be dissolved in it?" Five alloys were cast, the compositions aimed at being 1, 2, 3, 4, and 5 per cent. of bismuth, the ratio of copper to zinc being 52 : 48. In all the alloys to be described this—the eutectoid—ratio was always chosen. The alloys were cast in small chill moulds, $\frac{5}{8}$ inch diameter, and weighed about 300 grammes. Those containing approximately 1, 2, 4, and 5 per cent. of bismuth showed the typical structure of apparent β , the only noticeable effect being a diminution in the size of the β areas with increase of bismuth. No traces of bismuth could be seen in any of these. It is remarkable that apparent β should be able to dissolve about 5 per cent. of a metal which is quite insoluble in either of the constituent metals, copper and zinc. The structure of this alloy is shown in Plate XIV. No. 3.

With the 3 per cent. (actually 2.90 per cent.) bismuth alloy, however, the case was different. This showed the typical β areas as regards size, *but the entire interiors were seen to have been resolved into light yellow α and light blue γ , visible at a magnification of 100 diameters.* Moreover, in contradistinction to the other four alloys, which were tough, this alloy was quite brittle. This was the result that had been hoped for, and in this particular experiment the crystallizing influence of bismuth, instead of being overpowered as in the other four cases, produced a marked and complete development of coarse α and γ throughout the section. This development is shown in Plate XIII. No. 2.

As a matter of fact, no precautions had been taken to keep this alloy cool during its preliminary grinding before polishing, whereas the remaining four had been dipped in water from time to time. In order to test whether the heat of friction had caused this separation of α and γ , another specimen of the 2.90 per cent. alloy was ground with the same precautions.

The result, however, was the same—a complete structural development of α and γ . On the other hand, a specimen of the 5 per cent. alloy ground without any cooling precautions showed a decided development of α and γ in various places.

In order to see at what temperature crystallization of α and γ could be induced, the five samples were annealed at 115°C . for $2\frac{1}{2}$ days. After this treatment the 1 and 4 per cent. bismuth alloys remained unaltered, whereas the 2 and 5 per cent. showed distinct signs of α and γ development. The 2.90 per cent. alloy was unchanged. The series was then annealed at 180°C . for two days, and after this all of them showed signs of the breaking down of the apparent β into $\alpha + \gamma$. Plate XIII. No. 1 shows this stage in the case of the 1 per cent. alloy. The special interest of this photograph is that it shows some unaltered β (half-tone on the right-hand side), together with the decomposition products $\alpha + \gamma$, which appear as minute white and black specks chiefly on the left-hand side. Finally, an alloy was made containing about 10 per cent. of bismuth. This could be sawn, filed, and stamped quite readily. Thus the solvent properties of apparent β for a highly brittle and crystalline metal like bismuth are remarkable. This alloy contained a considerable amount of free bismuth distributed in small specks, as shown in Plate XIV. No. 4.

It follows from these experiments that, with one exception, bismuth did not produce a crystallization of α and γ from apparent β visible at low magnifications, but that its own highly developed tendency to crystallization was masked by the solvent properties of this substance. In the case of the exception—viz. the 2.90 per cent. alloy—however, the resolution of β into $\alpha + \gamma$ was most marked. Further, annealing at a comparatively low temperature (below 200°C .) was sufficient to cause the break-down of apparent β in all the alloys.

In considering reasons for the comparative ineffectiveness of bismuth, it is probably not incorrect to attribute this partly to its low freezing point, viz. 269.5°C . This is 200°C . below the temperature of the $\alpha + \gamma$ formation from β , so that the crystallizing influence of bismuth cannot be exerted on the complex at the moment of its formation (see, however, the effect of chromium). An important practical point to be

noted is that the moment the structure of apparent β was destroyed and replaced by $\alpha + \gamma$ visible at low magnifications, brittleness set in.

2. *Lead.*

This metal is insoluble either in copper or zinc, the metals being only partially miscible in the liquid state. From the practical standpoint it was important to investigate its influence thoroughly, because it is almost invariably present in greater or less amount in industrial brasses. Seven alloys were made, containing approximately 1, 2, 3, 4, 5, 10, and 20 per cent. of lead. None of them as cast showed any $\alpha + \gamma$ visible at low magnifications. They presented the structure of typical β areas, and most of them showed small black specks, which were probably lead. Plate XV. No. 5 shows the β structure of an alloy as cast containing 3.28 per cent. of lead. None of these alloys were brittle.

They were annealed for three days at 270° C., but showed no structural change. Afterwards they were annealed for nine days at 310° C., just below the freezing point of lead, but with no other change than that the β areas tended to *diminish in size*. This is a not unimportant point, because it is probably the first stage in the resolution of apparent β into $\alpha + \gamma$. But other than this no change was detectible.

It appears, therefore, that lead is almost, if not quite, without effect on the structural stability of apparent β , and, in view of its frequent occurrence in industrial brasses, this is a most important and valuable result, since it explains why comparatively large amounts of this metal can be used with impunity. Here, as in the case of bismuth, it is probably correct to regard the low freezing point of lead as being to some extent the cause of its ineffectiveness, since it solidifies about 140° C. below the temperature at which α and γ are produced.

3. *Chromium.*

This metal is not appreciably soluble either in copper or zinc, and on account of its characteristic crystallization and very high freezing point—about 1510° C.—it might have

been anticipated that it would aid the $\alpha + \gamma$ crystallization. Four alloys were cast, containing approximately 1, 3, 5, and 10 per cent. of chromium. The first two showed typical β areas. The 5 per cent. alloy showed in addition a small number of white spots, presumably consisting of undissolved chromium. The 10 per cent. alloy showed a larger number of these spots and principally β areas. Here and there, however, there were very distinct indications that the structural resolution into $\alpha + \gamma$ had occurred. The alloys were then annealed for ten days at 400° C., but this produced no appreciable effect on their structure. Thus it appears that it is only with high percentages that chromium exerts a structural influence on apparent β in producing $\alpha + \gamma$ visible at low magnifications. The above alloys were not brittle, but very hard to saw.

Summarising the insoluble metals, bismuth, lead, and chromium, it may be said, with the exception of one bismuth alloy, that their effects on the structural stability of apparent β are very slight. Certainly the percentages of lead and bismuth ordinarily present in industrial alloys will be quite without influence, and this result is important, because it can be safely concluded that they will not have an embrittling effect of the above kind.

CLASS II.—METALS OF PARTIAL SOLUBILITY.

4. *Antimony.*

Antimony forms with copper the compound Cu_3Sb at the copper end of the binary series, which, however, appears to be quite insoluble in copper. With zinc it forms the compounds SbZn and Sb_2Zn_3 . Its possible influence, therefore, on the stability of apparent β is very difficult to forecast. These compounds crystallize in well-defined forms. Two alloys were made, containing approximately 1 and 2 per cent. of antimony. On examining these it was clear that this metal had displaced the β from the eutectoid composition, and had caused the separation of a marked amount of γ , which appeared as light blue spots distributed evenly among the reddish-brown β

crystals in the case of the 2 per cent. alloy. Plate XV. No. 6 shows this structure in which the γ specks appear white. The displacement was naturally less in the 1 per cent. alloy, and here the γ was confined chiefly to the crystal boundaries, appearing in the form of a thin cement built up of a number of γ particles. These alloys are quite brittle.

5. *Tin.*

Copper can dissolve up to about 13 per cent. of tin, forming what may be called α -tin cuprite. Zinc and tin, however, are quite insoluble in one another, and form a eutectiferous series of alloys from one side of the diagram to the other.

An alloy was cast designed to contain 1 per cent. of tin. It was quite brittle. On examining its structure there was found to be an enormous development of γ (light blue) crystals of characteristic form on a gold ground (evidently α). The structure is shown on Plate XVI. No. 7, and the boundaries of the original β crystals are clearly seen. In this case, therefore, 1 per cent. of tin had been sufficient to destroy the structural stability of apparent β , and by throwing the composition on the γ side of the eutectoid point it had caused a very considerable proportion of the total γ present to separate out, leaving a residue principally of α . Actually this alloy contained rather less than 1 per cent. of tin (0.995 per cent.).

6. *Aluminium.*

The effect of aluminium has been dealt with in the author's previous paper* (Plate XIII. Nos. 19 and 20).

The precipitation of γ is well seen in No. 20.

7. *Vanadium.*

This metal was found to be most powerful in precipitating $\alpha + \gamma$ from apparent β . Plate XVI. No. 8 shows the structure of an alloy containing not more than 0.95 per cent. of vanadium made from cupro-vanadium, copper, and zinc. An

* *Journal of the Institute of Metals*, No. 1, 1912, vol. vii, pp. 85-87.

inspection of this shows parts of the boundaries of five originally β crystals. The crystals themselves are seen to have been resolved into approximately equal parts of γ crystals, which appear dark, and α crystals, which appear white. In the original specimen these possess the characteristic light blue and gold colours respectively. In its completeness this recalls the case of the 2.9 per cent. bismuth alloy and also the 1 per cent. silicon alloy which follows. The alloy was not very brittle, but considerably harder than an apparent β alloy.

8. *Silicon.*

Not less potent in producing the characteristic resolution into α and γ is the element silicon. This is evident from Plate XVII. No. 9, which shows the structure of an alloy containing 1.19 per cent. of silicon, which has been polished but not etched. In this the light blue γ crystallites stand in relief owing to their superior hardness, and appear white with dark edges. These are embedded in a matrix of golden α , which also appears white. The resolution of apparent β into $\alpha + \gamma$ appears to be complete. This alloy was made by melting together portions of cupro-silicon, copper, and zinc. Like the vanadium alloy, it was not brittle, but hard to saw.

9. *Iron.*

This metal occupies a transition place between Classes I. and II., and constitutes a link between them. On the one hand, it appears to be insoluble in zinc; on the other hand, copper can retain about 3 per cent. of it in solid solution. Alloys designed to contain 1 and 3 per cent. of iron were made from a ferro-copper containing 5.66 per cent. of iron. They were hard, but not brittle. Both of them showed typical areas of apparent β . They were annealed for nine days at 420° C.

The 1 per cent. alloy was unchanged after this treatment, whereas the alloy containing 2.75 per cent. of iron showed numerous places where a breaking down of the apparent β crystals had begun. There was also a good deal of pitting,

indicating that a brittle constituent—presumably γ —had been removed in polishing. Plate XVII. No. 10 shows the structure of this alloy polished but unetched. A β area undergoing decomposition is seen near the centre of the field. When taken out of the furnace the surface of this alloy appeared markedly crystalline, and of a most brilliant yellow colour.

It is clear from these experiments that any industrial β alloy, especially if it is likely to be heated in practice, should not contain more than 1.5 to 2 per cent. of iron, otherwise the apparent β structure, upon which its valuable properties depend, will be in danger of being destroyed and brittleness will ensue.

The effects of the metals in this class may be summarised as follows:—

All of them act in the direction of precipitating $\alpha + \gamma$ visible at low magnifications from apparent β , and the rationale of their action appears to be that they displace the alloy from the eutectoid composition and shift it to the γ side. In consequence of this a certain excess of γ is present, and accordingly γ crystallites are produced, leaving a residue of α . This is particularly noticeable in the cases of antimony, tin, aluminium, vanadium, and silicon. Much the slowest metal in its action is iron, and this metal is one of the least soluble in copper and zinc of the series. Up to about 1.5 to 2 per cent. it is almost without effect, and this is the reason why it can be used with such advantage in the special iron brasses such as the δ metals. It may be conveniently regarded as forming a connecting link between Classes I. and II.

CLASS III.—VERY SOLUBLE METALS.

10. *Nickel*.

Copper and nickel are completely miscible in all proportions, and although zinc does not dissolve appreciable quantities of nickel, the latter dissolves as much as 35 per cent. of the former. Moreover, the mutual solubility of these three metals is well instanced in the German silvers, which consist of a

single solid solution. In these cases, however, the proportions of copper and zinc are not those of the β constituent. Five alloys were cast, designed to contain 1, 3, 5, $7\frac{1}{2}$, and 10 per cent. of nickel. Of these the 1 and 5 per cent. alloys were found to possess the β structure. Rather curiously the 3 per cent. alloy was seen to have been completely resolved into $\alpha + \gamma$. This result is shown in Plate XVIII. No. 12, the exact nickel percentage being 2.79. Parts of four originally β areas are seen whose interiors now consist of the $\alpha + \gamma$ complex. This instance of a decomposition occurring in an anomalous position recalls that of the corresponding bismuth alloy (p. 61). The $7\frac{1}{2}$ per cent. alloy consisted almost entirely of apparent β crystals, but there were indications of the separation of another constituent, which appears white (Plate XIX. No. 13). The fifth alloy, which contained 9.25 per cent. of nickel, was found to have been resolved in the striking manner shown in Plate XIX. No. 14. None of these alloys were brittle, but they were harder than pure copper-zinc β .

In order to test the stability of the apparent β structure of the 1 per cent. alloy it was annealed for ten days at 420°C . The result is shown in Plate XVIII. No. 11. Decomposition has set in and advanced considerably, and recalls that of the 1 per cent. bismuth alloy in its general character. Light and dark resolution products are seen on a half-tone ground. The latter is probably β , but which of the remainder is α and which γ it is impossible to say.

It is clear from the above experiments that nickel, in spite of its solubility for copper and zinc, not only does not retard the $\alpha + \gamma$ resolution, but aids it considerably.

11. *Manganese.*

Manganese and copper are soluble in all proportions, but the equilibrium diagram of the manganese-zinc system has not been determined, and the mutual solubilities of these metals are unknown. Alloys designed to contain 1, 3, and 5 per cent. of manganese were cast from a cupro-manganese, copper, and zinc. On examination each of them possessed the typical β structure. They were tough, but not brittle.

For ten days they were annealed at 400° C. and again examined. After this treatment no signs of α and γ could be detected, the only difference being that the apparent β crystals were much smaller. (The author has concluded from his experiments on the resolution of the pure constituent that this is really the first step in the decomposition into $\alpha + \gamma$ visible at low magnifications.)

As regards the metals of Class III., nickel, though somewhat irregular in its action, behaves like the majority of the metals of Class II., and aids the $\alpha + \gamma$ separation by displacing the alloy on to the γ side of the eutectoid point. Manganese, on the other hand, is almost without action of this kind, and this explains why it can be used with advantage in the manganese brasses, since it toughens the alloys without making them brittle.

Before concluding the investigation it was considered important to test whether certain of the above metals, which were found to have either no, or at most only a slight, influence on the structural stability of apparent β , lowered the temperature of the $\beta \rightarrow \alpha + \gamma$ change.

The metals tested were chromium, iron, and manganese, one from each class, since at any rate two of them have a beneficial effect on the properties of the brasses. Accordingly both heating and cooling curves were taken of alloys containing about 3 per cent. of these metals. The cooling curves are reproduced in Fig. 1, and the results tabulated below, the figures for pure β being added for purposes of comparison.

Composition.	Heating Curve, Degrees Centigrade.	Cooling Curve, Degrees Centigrade.	Mean Temperature, Degrees Centigrade.
3.01 per cent. chromium .	462	450	456
2.75 " iron .	456	444	450
3.12 " manganese .	450	438	444
Pure β . . .	470	457	463

These figures are very interesting. They show that all three metals are almost without influence on the inversion. The

mean lowering is only 7° with chromium, 13° with iron, and 19° with manganese. Not only so, but the characters of the curves are very similar to one another, and to that given by pure β . Only in the case of manganese is the critical interval somewhat widened and the sharpness of the peak diminished.

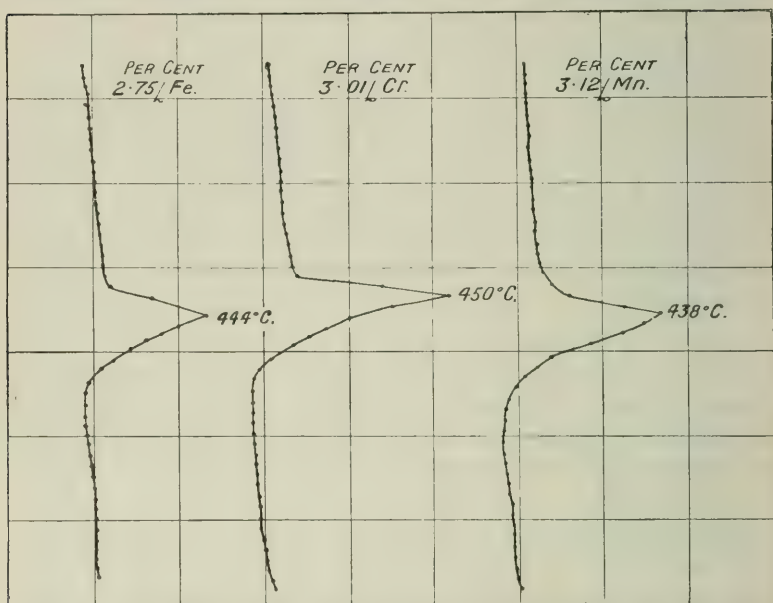


FIG. 1.—Derived Differential Cooling Curves.

Thus the temperature and character of the inversion are almost independent of the foreign metal. Taking these results into consideration with those obtained with aluminium by Mr. Edwards and the author,* it seems unlikely that any element will lower the temperature of the inversion below the ordinary temperature so that β will be the stable phase, and this conclusion is of the greatest practical import.

PRACTICAL CONSEQUENCES.

The foregoing investigation has been carried out by the author in fulfilment of a pledge given at the end of his joint

* *International Journal of Metallography*, 1912.

paper with Mr. Edwards, published in 1911,* and stated in the following words: "The important practical problem arising out of the above discovery is as follows: 'Is it possible to suppress the critical point at 470° C. by the introduction of some element or elements into the copper-zinc alloys, and thus to avoid the formation of γ and its consequent brittleness?' If this difficulty can be overcome the consequences will be far reaching. It is the author's intention to take up this investigation without delay."

In the light of the foregoing investigation this question must now be answered in the negative. There is no element of the eleven investigated which suppresses the change. On the contrary, the majority of them aid it. Such metals are tin, antimony, vanadium, nickel, aluminium, and silicon, and these complete the $\beta \rightarrow \alpha + \gamma$ structural change in a remarkable manner. To a lesser extent the metals iron, chromium, and bismuth act in the same direction. Only lead and manganese appear to be almost, if not quite, without action. The problem therefore of making β the stable phase at the ordinary temperature appears to be theoretically insoluble.

The result of the author's investigations on the β constituent is not, however, the complete failure that the above paragraph appears to indicate. In another paper on the subject the extraordinary structural stability of the apparent β phase, consisting only of copper and zinc, is emphasized,† and this in reality constitutes the practical solution of the above problem—viz. *the stability of the β structure can be strengthened, not by adding foreign elements, but by removing them as completely as possible.*

The industrial copper-zinc alloys containing apparent β may be grouped under the general heading of Muntz metals. From a constitutional standpoint these consist of massive or coarse α together with eutectoid $\alpha + \gamma$, i.e. apparent β . Provided that any given alloy does not require to be heated in use it can be rendered structurally most stable by preparing it from copper and zinc which contain as few impurities as possible.

* *Journal of the Institute of Metals*, No. 1, 1911, vol. v, p. 148.

† "The Structural Resolution of the Pure Copper-zinc β Constituent into $\alpha + \gamma$," page 52. (Paper presented at the same meeting.)

It will then be in the most stable condition it is possible to realise practically. The system is not of course as stable as one consisting only of apparent β . The massive α is the predisposing cause of structural instability, but at ordinary temperatures its effect on the $\alpha + \gamma$ complex is negligible, since molecular mobility at this temperature is very slight. The two structural elements will exist side by side almost, if not quite, indefinitely.

The case, however, is different if the alloy is required to be heated in use. As the temperature rises so also does the molecular mobility, and in such cases there will be a tendency for the α in the $\alpha + \gamma$ complex to diffuse and be absorbed by the massive α in the alloy. This must have its consequence, the coalescence of γ into coarse particles, and with this brittleness will set in.

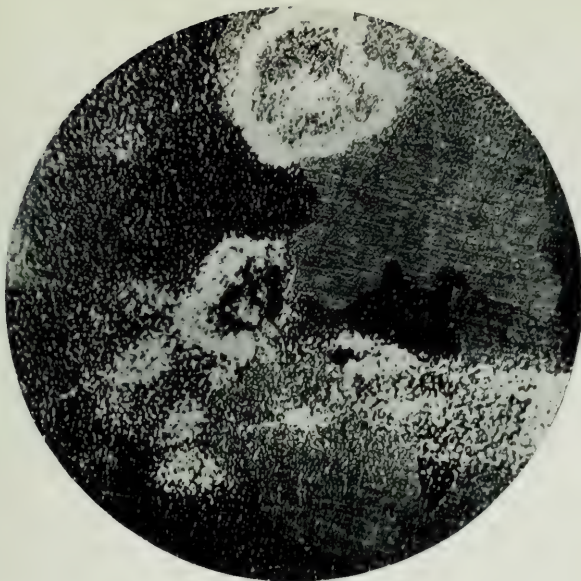
The author acknowledges with pleasure the assistance of Mr. T. West, M.Sc., in most of the experiments described in this paper.

SUMMARY.

The influence of various common metals on the structure of the apparent β constituent in copper-zinc alloys has been determined.

Class I.—Metals insoluble in copper or zinc, viz. bismuth, lead, and chromium. With the exception of one alloy, containing 2.9 per cent. of bismuth, their effects on the structural stability of apparent β were found to be very slight, and the conclusion is warranted that the percentages of lead and bismuth ordinarily present in industrial alloys are entirely without influence.

Class II.—Metals of somewhat limited solubility, viz. iron, antimony, tin, aluminium, silicon, and vanadium. With the exception of iron, all these metals aid the precipitation of $\alpha + \gamma$ visible at low magnifications from apparent β . They displace the alloy from the eutectoid composition, and shift it to the γ side. Consequently γ crystallites are produced, leaving a matrix of α . Iron is very much slower in its action, and up to about 2 per cent. is without effect. It forms a connecting link between Classes I. and II.



No. 1.

Bi=1.05 per cent. ; Cu=50.92 per cent. ; Zn=47.65 per cent.

Structure after annealing for two days at 180° C. Apparent β (chiefly on right-hand side) appears half tone. $\alpha + \gamma$ appears as black and white specks. Magnified 150 diameters.



No. 2.

Bi=2.90 per cent. ; Cu=49.72 per cent. ; Zn=47.21 per cent.

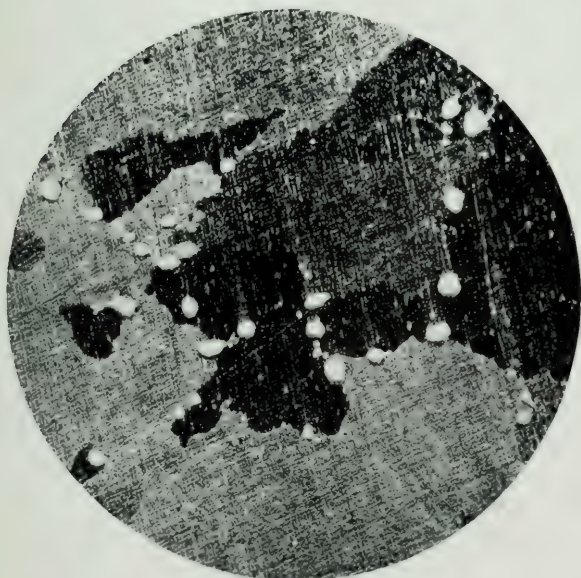
Structure of alloy as cast, showing complete resolution of apparent β into α (yellow), which appears white, and γ (light blue), which appears dark. Magnified 150 diameters.



No. 3.

Bi=4.77 per cent. ; Cu=49.57 per cent. ; Zn=45.47 per cent.

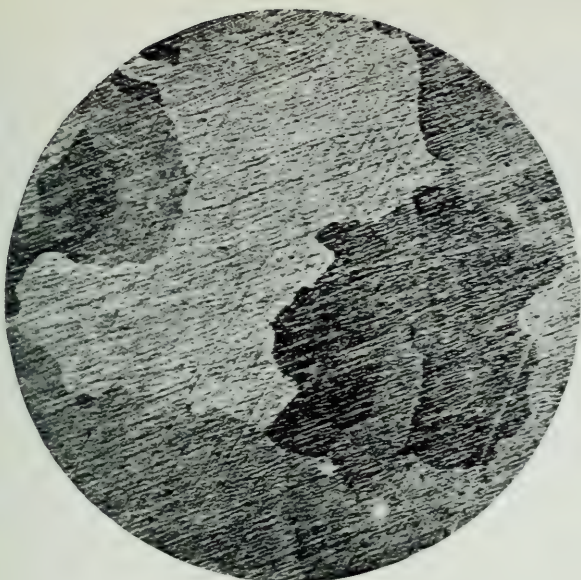
Structure of alloy as cast, showing solvent properties of apparent β for bismuth. Magnified 150 diameters.



No. 4.

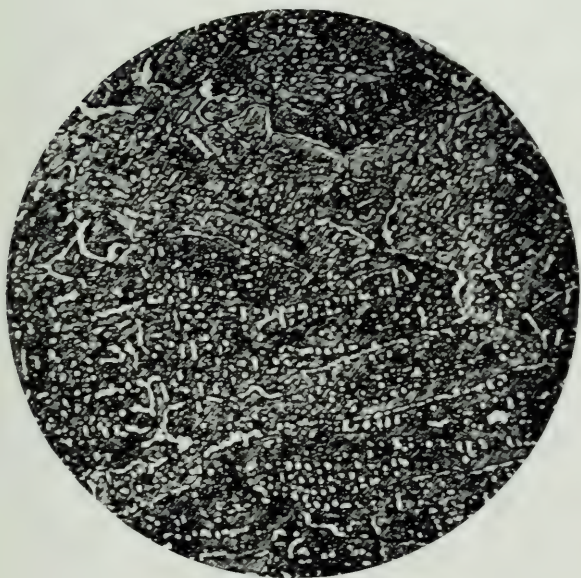
Bi=9.23 per cent.

Structure of alloy as cast. The white spots represent free bismuth, the remainder apparent β . Magnified 150 diameters.



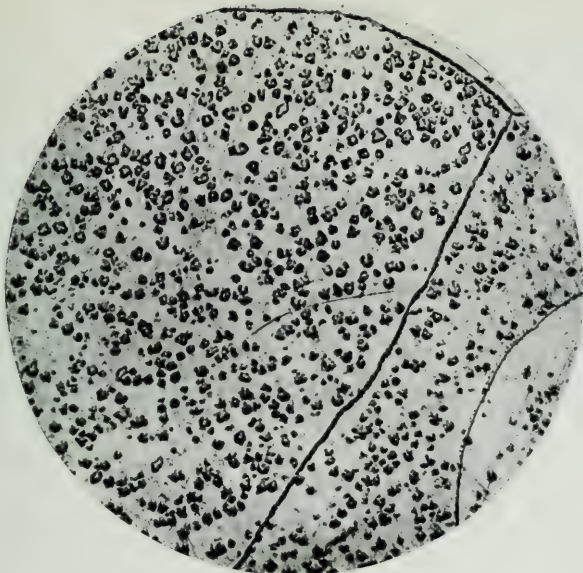
No. 5.

Pb=3.28 per cent. ; Cu=51.05 per cent. ; Zn=45.97 per cent.
 Structure of alloy as cast, showing solubility of lead in apparent β .
 Magnified 150 diameters.



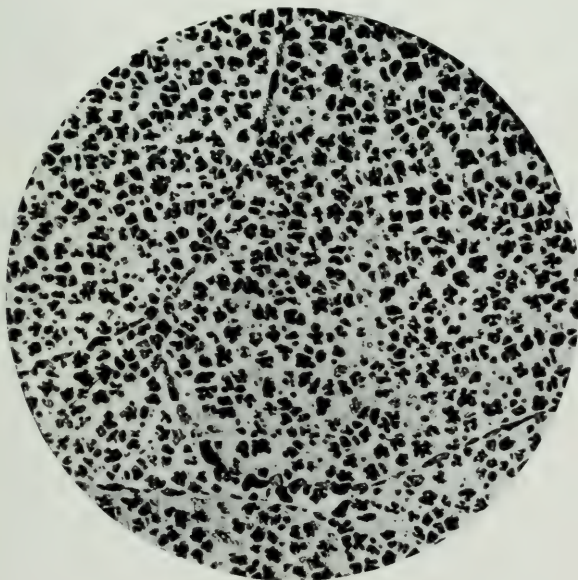
No. 6.

Sb=1.90 per cent. ; Cu=50.37 per cent. ; Zn=47.70 per cent.
 Structure of cast alloy showing γ specks (which appear white) distributed
 through dark β . Magnified 150 diameters.



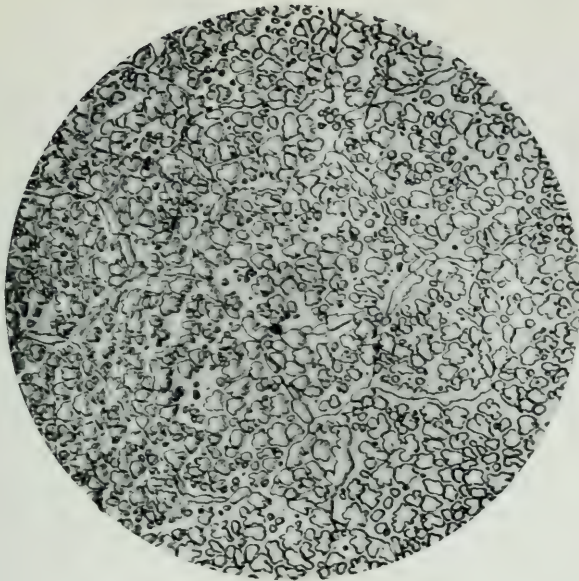
No. 7.

Sn=0.995 per cent. ; Cu=51.50 per cent. ; Zn=47.36 per cent.
Structure of cast alloy showing γ (small dark crystals) in a matrix of α (light). Magnified 150 diameters.



No. 8.

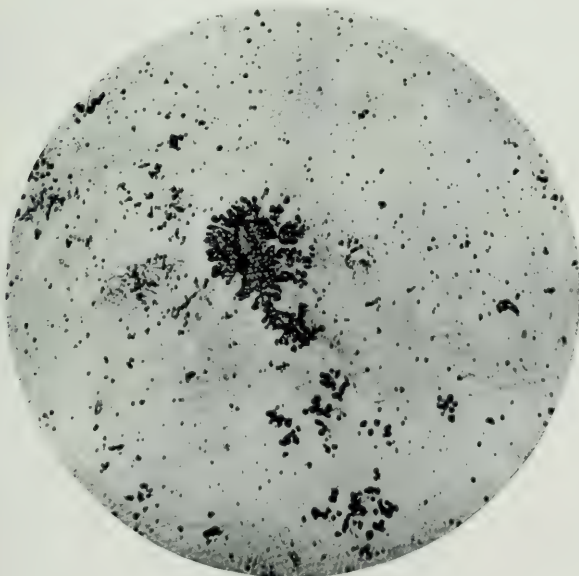
V=0.95 per cent. ; Cu=51.25 per cent. ; Zn=47.80 per cent.
(*By difference.*)
Structure of alloy as cast, showing complete resolution into γ crystallites (dark) and α (white). Magnified 150 diameters.



No. 9.

Si=1.19 per cent. ; Cu=51.05 per cent. ; Zn=47.70 per cent.

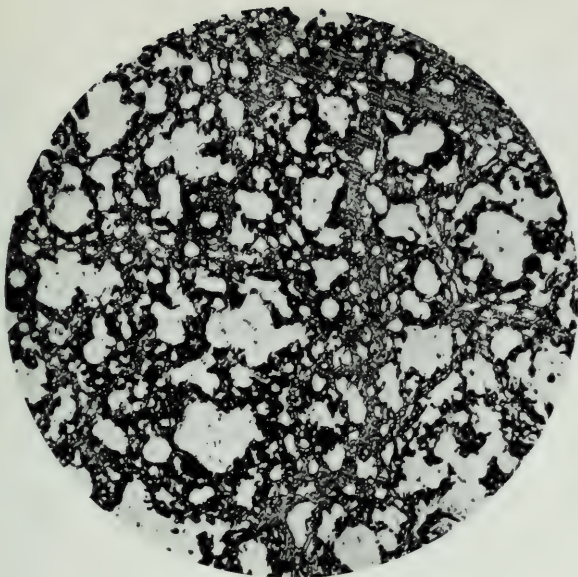
Structure of alloy as cast and polished, but unetched, showing γ crystal-lites (white with black edges) in a matrix of α (white). Magnified 150 diameters.



No. 10.

Fe=2.75 per cent. ; Cu=51.31 per cent. ; Zn=45.75 per cent.

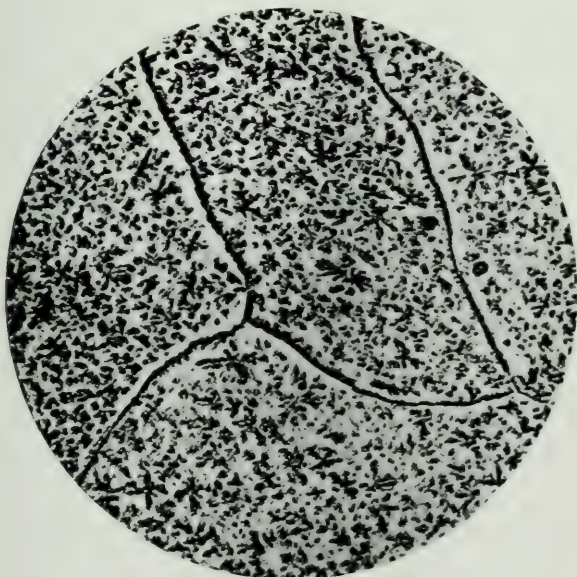
Structure of alloy after nine days' annealing at 420° C. (polished, but un-etched), showing an area near the centre where the resolution of apparent β has begun. Magnified 150 diameters.



No. 11.

Ni=0.96 per cent. ; Cu=51.90 per cent. ; Zn=47.09 per cent.

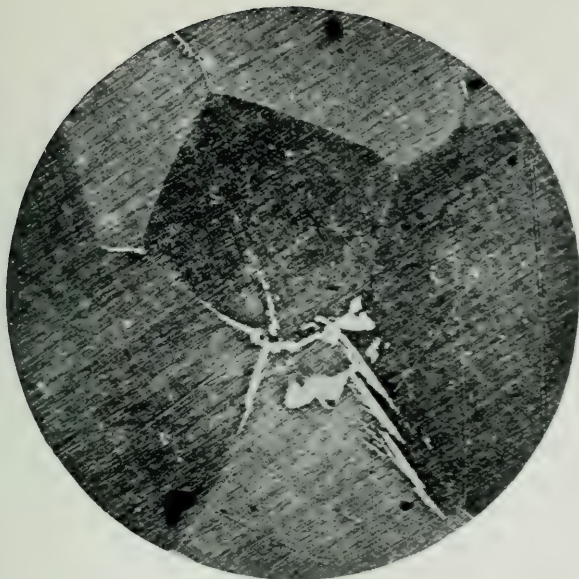
Structure of alloy after ten days' annealing at 420° C., showing the early stages of decomposition of the apparent β constituent. Magnified 150 diameters.



No. 12.

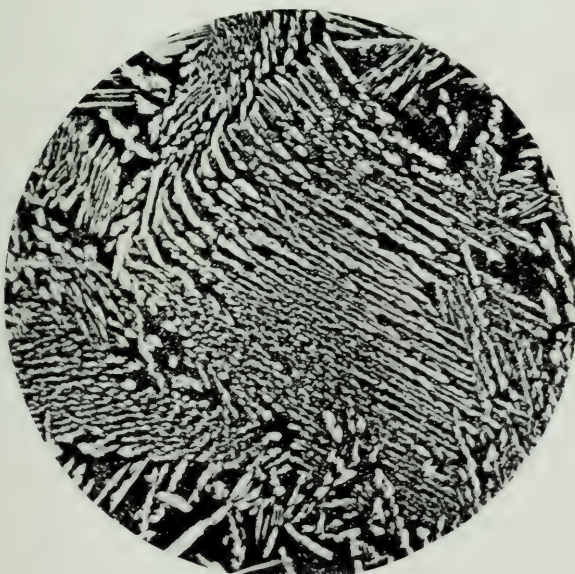
Ni=2.79 per cent. ; Cu=50.57 per cent. ; Zn=46.55 per cent.

Structure of alloy as cast, showing complete decomposition into γ (dark) and α (light). Magnified 150 diameters.



No. 13.

Ni=6.99 per cent. ; Cu=47.54 per cent. ; Zn=45.31 per cent.
Structure of alloy as cast, consisting almost wholly of apparent β .
Magnified 150 diameters.



No. 14.

Ni=9.25 per cent. ; Cu=46.59 per cent. ; Zn=43.98 per cent.
Structure of alloy as cast, showing complete resolution of β constituent.
Magnified 150 diameters.

Class III.—Metals of great solubility, viz. nickel and manganese. Nickel is somewhat irregular in its action, but behaves like the majority of the metals in Class II., whereas manganese is almost without action of this kind.

The metals iron, chromium, and manganese have only a slight influence on the temperature of the β to $\alpha + \gamma$ inversion. No metal has been found capable of lowering this transformation below the ordinary temperature.

The problem of making β the stable phase at the ordinary temperature appears to be theoretically insoluble. Practically, however, the structural stability of apparent β can be strengthened by keeping down the impurities in copper-zinc alloys to a minimum.

Provided that such alloys are not heated in use their stability will last practically for an indefinite period.

THE UNIVERSITY,
MANCHESTER.

JOINT DISCUSSION.

Dr. WALTER RÖSENHAIN (Member of Council), in opening the joint discussion on Professor Carpenter's two papers, said he thought that these were very interesting developments of papers that had previously been laid before the Institute, but they did not lend themselves to much discussion. They consisted of statements of experimental fact, and as far as he could see there was only one deduction from the facts which was at all open to discussion, namely, the suggestion that the general view that crystals of a duplex substance were bound to aggregate into larger units in the course of time was not universally tenable. Unfortunately that was contrary to the general principles of thermo-dynamics. He was afraid that even the example the author had taken so much trouble to furnish was insufficient for upsetting those general principles, and some other explanation would have to be found of that special case rather than to attempt to overthrow a generalization of that sort which was very well founded, not only on theoretical principles but on a very large number of facts. The only suggestion he could make at the moment was whether it would not be wiser for the author to assume that the β constituent when pure did not decompose. He thought it was just as easy, in fact a good deal easier, to reconcile that view with general theoretical principles and with other observed facts—apart from that special group—than to suppose that it was a duplex substance which failed to obey the ordinary laws of duplex substances. From the practical point of view he thought it was exceedingly interesting to find that there was in the paper another ground for believing in the importance of keeping the copper-zinc alloys pure. He was very pleased to find support of that kind forthcoming from other grounds than those on which he had himself advocated the use of extremely pure materials.

Professor A. K. HUNTINGTON, Assoc.R.S.M. (Vice-President), said that in the reply to the discussion on the last paper that the author wrote on the subject Professor Carpenter allocated to him the genial task of "the devil's advocate." That subsequently made him consider what the devil's advocate was. A devil's advocate, he found, was a person appointed when somebody was about to be canonized to dispute that particular individual's right to be made a saint. Personally he would never for a moment have disputed the author's right to be made a saint. The curious part of the thing, however, was that now the author had changed over and become his own devil's advocate. In the first paper that had just been read the author had thrown overboard altogether the assumption that β would split up into α and γ . He had deliberately thrown that over, and had thus become his own devil's advocate. It seemed to him that was rather like the practice of a modern business firm, which not infrequently, when it found that one part of the business was not doing well, turned it into a separate concern in order that the main part of

the business might not suffer when the bad time came. The author had concentrated the rest of his business in the second paper, which, however, he was afraid would not stand very careful analysis. A number of the cases that the author gave were cases which had come under his (Professor Huntington's) own personal notice during the last few years, and he had not the slightest hesitation in saying that they were cases where the constituents pushed the metal into the γ phase. He thought when the author came to look more carefully into that point he would realise that that was so. For instance, he would take the cases where a lot of γ was obtained—where the author had added silicon. The author had already got nearly 48 per cent. of zinc, which was the limit on one side of the β range, and he added 1.19 per cent. of silicon. On the authority of Guillet 1 per cent. of silicon was equivalent to 10 per cent. of zinc, a fact the approximate correctness of which had been substantiated by other workers. So that the author had carried it a long way into the γ region, and he thought it would be found that there would be about 45 per cent. of γ there due to the presence of the large amount of zinc, and the silicon. That at once disposed of the theory of the splitting up of the β into α and γ , for that alloy at any rate. All the cases which were given in the paper of which he knew anything told the same story. With regard to Photographs 13 and 14 in Plate XIX., both of them obviously contained α . There was no question about the white portion of those photographs being α ; and if the members looked at the amount of zinc present in No. 14 it would be found that it was 44 per cent., which was not in the γ region. It was not even in the β region, taking other things into account. He would not labour the point any further, but he thought it would be found that the resolution of β into α and γ did not take place, and that the appearances were due to other causes.

Professor T. TURNER, M.Sc. (Honorary Treasurer), said the paper was one which did not lend itself very much to criticism from one who had not actually seen the samples which the author had prepared. There were, however, several things which were of interest to practical men, so far as the results were concerned. One point, which had been mentioned by Dr. Rosenhain, was that brittleness of worked brass could not be removed by adding any other known impurity, and that the way in which the quality of the material had to be improved was rather by obtaining greater purity than by attempting to add other elements. He was very much interested in the differential cooling curves given on page 70, because they showed quite distinctly that it was impracticable to do away with the brittle range at about 470° C. That brittleness was a very useful property of these alloys for some purposes, but it was a disadvantage for others. Apparently, however, the author thought the brittle range would persist despite the character or quantity of the addition. From the point of view of the ordinary reader it might, perhaps, be well to insist upon the meaning of the word

"solubility" as used by the author in his papers. If two metals—such, for instance, as copper and bismuth, or zinc and iron—were melted together, it was found that they were soluble in each other. They might, perhaps, form what used to be called "ideal" alloys, or alloys which exist only within certain elevated ranges of temperature, but those metals were for all practical purposes soluble. They were, however, insoluble structurally, *i.e.* in the cold metal and as viewed under the microscope. For example, to merely state that iron was insoluble in zinc might be quite true from a metallographic point of view, but from the point of view of the practical man it was incorrect, because there were well-known alloys—the compounds of zinc and iron—which were soluble in zinc, otherwise they could not get the ordinary hard zinc of commerce. He had read the paper with interest, and it evidently opened up questions which called for further discussion.

Dr. C. H. DESCH (Glasgow) said the last paper that the author presented to the Institute converted him to the view that his metastable diagram was substantially correct. That conclusion had not been modified after reading the present extremely interesting papers, but there were certain difficulties which still presented themselves. The non-resolution of pure β , except in the presence of an excess of α or γ , did not seem to him to justify the conclusion that pure apparent β was absolutely stable. Its condition might be metastable, but many metastable substances were extremely difficult to resolve. There were many instances in which such an undoubtedly metastable material as glass remained without devitrification for an indefinite time, but in the presence of suitable nuclei it was pretty rapidly resolved. A very peculiar effect that had been observed was the diminution in the size of crystals of the apparent β , as shown in Plate IX. in the first paper. In a pure metal, the change from large to small crystals on annealing would be in the direction of lesser stability, and not in the direction of greater stability. It seemed strange that the reverse occurred when they were dealing with a two-phase system. He did not know whether the author had any explanation to offer on that point, but it was certainly contrary to what one would expect. Then he wished to refer to a point in connection with Plate XVII. of the second paper, Photograph No. 9, which had already been referred to by Professor Huntington. In the structure in that photograph, if the formation of γ were entirely due to the cause suggested by Professor Huntington, the structure would be γ + apparent β , whereas, on the author's hypothesis, it consisted of γ + α . He desired to know whether there were any experimental means, in examining these microsections, of determining whether the ground-mass was α or apparent β . The same remark might be made with regard to Photograph No. 14 in Plate XIX., where the structure, as Professor Huntington said, had the appearance of a very typical α - β structure. If that were really an α - γ structure it was rather surprising that the metal did not show extreme brittleness.

Mr. O. F. HUDSON, M.Sc. (Birmingham), said he desired to ask, in connection with the example of large crystals of α and γ apparently occurring together in the same specimen (Plate XVI. Nos. 7 and 8), whether the author had considered the possibility of the diffusion of vanadium from the vanadium specimen into the pure specimen, because that was a point that might be of importance. The speaker had made some attempts to bring about the resolution of β into α and γ . He had annealed some alloys consisting of β , with a little α . In one particular case (and similar results were obtained with the other samples), after annealing the alloy for about eighteen hours there was a very decided growth of extra α ; but the alloy was still distinctly α and β . On further annealing for another fourteen days, there was apparently no further increase in the amount of α that had crystallized out, but the α crystals had increased very considerably in size. The alloy was still α and β , and the β had exactly the same appearance as in the original. The same thing applied to the β - γ alloys, but unfortunately he had not carried the annealings on for long enough to make them comparable with any of the author's. So far as he had gone, however, he quite agreed with the author's statement that it was exceedingly difficult to split β up into α and γ , and so far he had failed to do so. Finally, he desired to ask the author the same question that Dr. Desch had asked, namely, whether there was any method of distinguishing between α and β when either of them was in the presence of γ . For example, on looking at Photograph 12, Plate XVIII., in the second paper, he noticed it was called γ and α , but he wished to point out that it was typically a β - γ structure. It was exactly the structure that would be obtained with a pure alloy of, say, 49 of copper and 51 of zinc. He desired to know whether there were any means whereby it could be said with certainty that that constituent was α and not β .

Mr. LEONARD ARCHBUTT (Member of Council) asked the author whether, in view of the great difficulty which had been experienced in effecting the resolution of the β constituent, he was still of opinion that that change caused the brittleness which was sometimes found to occur in old brasses, such as the wire referred to in the author's and Mr. Edwards' paper, read before the Institute in January 1911. It seemed very strange that 3 per cent. of bismuth should effect a change which 1 per cent., 2 per cent., and even 4 per cent. and 5 per cent. did not bring about. Had the author confirmed that result by preparing another alloy containing 3 per cent. of bismuth, and proved that the same thing took place? In other words, was that observation a purely accidental occurrence, or was it one that always occurred when 3 per cent. of bismuth was present? It also struck him that it would be useful if the author were to try the effect of much smaller quantities of the elements instead of the very large quantities that were used, which were far beyond anything likely to be met with in commercial alloys.

Mr. T. VAUGHAN HUGHES, Assoc.R.S.M. (Birmingham), said he had not the pleasure of being present while the paper was being read, but he

had made an endeavour to assimilate it before the meeting, and felt very much in the position of one who had swallowed a very indigestible pill. He rose more for the purpose of asking one or two questions than of criticizing the paper. The first question he wished to ask was whether in the analyses of the alloys the author always made them after casting or after experiment. Were any results taken by difference? He was not quite certain from reading the paper through whether that had been always the case. The next question he desired to ask with regard to the photomicrographs was whether the author had examined the results under higher powers than 150, say up to 1000. Generally speaking, the total result of the paper to his mind was, that it required revision by other friends of the author's who had the time to devote to it, and it also opened up a series of investigations which was a matter of further discussion.

Professor CARPENTER, in reply, said that Dr. Rosenhain had stated, in dealing with the question of the resolution of the pure β constituent, that his (the author's) statement that the β structure was absolutely stable on prolonged annealing was contrary to the laws of thermo-dynamics; and Dr. Rosenhain had suggested as an alternative to that conclusion that in the pure β constituent the change into $\alpha + \gamma$ did not take place at all. The answer to that was, Why was it then that in the pure β constituent the maximum thermal inversion was obtained? Starting from the α side, the thermal inversion was quite well marked the moment that β appeared; it increased in intensity up to the pure β constituent; reached a maximum there; diminished with the addition of γ ; and finally disappeared when the γ constituent constituted the whole field. That seemed to him conclusive proof that the change was one which occurred in the pure β constituent, quite irrespective of α and γ . He had been very interested to notice in Dr. Desch's recent extensive monograph on "Diffusion in Solids" that there were two other metallic systems which somewhat approached the copper-zinc β constituent in regard to the apparent structural stability of a single phase. One was the nickel-iron eutectoid, plessite, which Dr. Benedicks showed, after prolonged experiments with artificially prepared alloys, was really a duplex constituent; and the other occurred in the cadmium-tin system recently worked upon by Dr. Guertler. In both those cases it was extremely difficult to resolve the structure of a material which was apparently homogeneous, but which there was every reason for thinking was eutectoid. Professor Huntington had just used his (the author's) paper, which he called "The effect of other metals on the structure of the β constituent in copper-zinc alloys," for a purpose he had never for a moment contemplated. Professor Huntington had attempted to represent the paper as an effort on his (the author's) part to prove that the β constituent consisted of α and γ . The paper had nothing whatever to do with that proof. That was given, to his mind, conclusively in his last paper, which dealt only with copper-zinc alloys, and in which the resolution into α and γ was obtained by having initially either a slight

excess of α or of γ . The answer to Professor Huntington's point was contained in the summary of the paper. Professor Huntington had pointed out—and quite truly—that the effect of the added metals, particularly silicon and vanadium, was to cause a large excess of γ to be formed. That was exactly what he (the author) pointed out, because if they would turn to page 72 they would find he said under Class II.: “With the exception of iron, all these metals aid the precipitation of $\alpha + \gamma$ visible at low magnifications from apparent β . They displace the alloy from the eutectoid composition, and shift it to the γ side.” With regard to Professor Turner's point as to the solubility of zinc and iron, the statement in the paper was based upon the diagram given in Guertler's “Metallography,” in which it was quite obvious that although zinc was soluble in iron to an appreciable extent the solubility line of an iron-zinc compound in zinc was practically nil. He also wished to point out that it was not a question of iron, but of an iron-zinc compound being soluble in zinc. Coming to Dr. Desch's remarks and the question as to whether the β constituent must be regarded as being metastable below the inversion temperature, there he thought it was necessary to distinguish between constitutional and the structural stability. Constitutionally there was absolutely no reason for thinking that it was metastable. It had undergone the inversion into $\alpha + \gamma$; but structurally it was metastable, and from that point of view it was the most extraordinary metastability of which he had had experience. But the metastability was only permanent in the absence of either α or γ . He regretted he could not answer Dr. Desch's question with regard to the diminution of the size of the apparent β crystals after prolonged annealing, but there was one point to which he thought Mr. Hudson had called attention in the last discussion which was worth noting, namely, that whereas the majority of solid solutions after annealing developed twin crystals the apparent β constituent never did. That was a noteworthy point, and seemed to place this constituent in a special class. With regard to the micrographic distinction between α and β , he had, at the request of the Council, brought with him some of his specimens, and he would be very pleased to show any of the members, who were specially interested in the subject, specimens of the majority of alloys referred to in the paper. It was extremely difficult to convey by photographs all the evidence which could be seen under the microscope itself. With regard to the colour, there was no doubt as to the difference between α and β when one was really accustomed to working with them, as he had been for more than two years. The colour of α was bright yellow; that of β was reddish-brown. In the segregation of either α or γ there was a gradual transition from brown to yellow. In the transitional stage the etching phenomena were very puzzling. The true colours of α and γ were only obtained in the completely annealed specimens. He quite agreed with Mr. Hudson's remarks with regard to the annealing of the specimens. Nobody knew better than he did that it was a tedious matter to anneal them, but he thought if Mr. Hudson were to prolong the annealings to the extent that he

(the author) had done, he would find that he obtained the complete α and γ segregation. He thought the fourteen-day period mentioned by Mr. Hudson was not sufficient in which to complete it. With regard to Mr. Archbutt's point as to brittleness, he would be very much obliged if that gentleman would repeat his question, because he had not quite grasped it.

Mr. ARCHBUTT said he desired to know whether the difficulty that the author found in bringing about the resolution of the β constituent by prolonged annealing, which was practically stable in the absence of other impurities, had altered his views as to the cause of the brittleness of brasses which had been kept for a number of years.

Professor CARPENTER inquired what composition Mr. Archbutt was referring to.

Mr. ARCHBUTT replied that he was referring to a composition the analysis of which the author had given.

Professor CARPENTER inquired whether Mr. Archbutt was referring to his original paper with Mr. Edwards.

Mr. ARCHBUTT said he did not remember what impurities were present. It was one of Professor Forbes' specimens.

Professor CARPENTER asked how much copper and how much zinc there were in the alloy.

Mr. ARCHBUTT replied that he did not remember.

Professor CARPENTER presumed Mr. Archbutt was referring to the first paper by Mr. Edwards and himself.

Mr. ARCHBUTT replied in the affirmative.

Professor CARPENTER said he was not dealing with that for the moment, because that alloy contained no structurally free β . It was just on the α limit, and that was not quite the same question. With regard to Mr. Archbutt's question as to the separation of α and γ in the 3 per cent. bismuth alloy, he regarded it as an accident of casting that the 1 and 2 per cent. and the $4\frac{1}{2}$ per cent. did not show this, and that the 3 per cent. did. But as he pointed out in the paper, on annealing at a comparatively low temperature, every one of the four deposited the α and γ . Then as to the percentages of foreign metals added, these varied from small to large amounts in several instances. As far as the industrial brasses were concerned, and the impurities they were liable to contain in the shape of bismuth and lead, he thought the experiments showed that even the largest amounts would have no influence at all in destroying the apparent β structure.

Mr. ARCHBUTT asked what was the case with regard to tin.

Professor CARPENTER said that tin was not put in industrially as an impurity. It was added on purpose, and not to the Muntz metals, but to the condenser tube metals. There was no free β present in that case.

Mr. J. H. BARKER said there was in vanadium-bronze made, for instance, by the Parsons Company. Up to $1\frac{1}{2}$ per cent. of tin was there obtained, and that was largely β .

Professor CARPENTER said he did not know the composition of the alloy that had been mentioned.

Mr. ARCHBUTT said he understood the author found that tin was one of the metals that had a tendency to cause the inversion.

Professor CARPENTER said that was the case. Mr. Vaughan Hughes had asked a question as to the methods of analysis, and as to whether any figures had been taken by difference. Every element had been estimated directly, except vanadium. The vanadium alloy was estimated by difference. As far as he knew a good method did not exist of estimating vanadium directly in such alloys, or if it did he would be very glad if any members would inform him what it was.

Professor HUNTINGTON asked whether aluminium was looked for in the vanadium alloy.

Professor CARPENTER replied in the negative. Mr. Vaughan Hughes also asked whether the alloys were investigated under higher magnifications. The answer was in the negative, because the whole object of the work had been to show the resolution of the β constituent at low powers. His original paper dealt with the structure of β under very high magnifications, and it was objected that if those changes took place the author ought to be able to show them at low magnifications. Therefore in the three subsequent papers a low magnification had been adopted.

He believed he had dealt with the main points which had been raised in the discussion, but if he had left any unanswered he would be glad to reply to them in writing.

The PRESIDENT, in proposing a hearty vote of thanks to the author for his extremely interesting communication, said there were one or two points in the paper in regard to which he would like to have further information. The author's statement that the effect of 1 per cent. of bismuth did not produce brittleness had very much surprised him. He remembered having a contract with the Chinese Government to produce 10 or 20 tons of coins of the composition of Muntz metal. The copper which was supplied to the works contained 0.3 per cent. of bismuth, and the bars of the alloy could not be rolled without breaking. The members knew that it was impossible to take bismuth out in an ordinary

copper-refining furnace, and he therefore sent the copper to a native Japanese works, where silver was removed from copper by liquation. The copper was melted with lead; the lead was allowed to liquefy out from the mixture, when it brought out the silver, and with the silver the bismuth. After that treatment no difficulty whatever was experienced in producing satisfactory bars. With larger percentages possibly a tough alloy could be obtained, but he was very much surprised that the metal was not brittle with 1 per cent. It might seem to many people that researches such as those which were being conducted by the author, Dr. Desch, and others were of little practical use. Speaking from the practical point of view, he considered them to be of the utmost value, for it must be borne in mind that most alloys were not mere mixtures of metals, but mixtures of groupings of metals; and the more we knew about the behaviour of those groupings and their constitution, the better we would be able to deal with alloys on a large scale. If rule of thumb and empiricism were to be got rid of in metal works, it could best be done by studying the inner structure of metals; at all events that had been his experience.

He would only refer, in confirmation of that statement, to the work which was now being done in the manufacture of iron and steel, where, in consequence of the researches into the structure of steel, the old empirical methods were being laid on one side, and all important operations were now conducted on scientific principles. In conclusion, he asked the members to accord a hearty vote of thanks to Professor Carpenter for his extremely interesting paper.

The resolution of thanks was carried with acclamation.

COMMUNICATIONS.

Professor A. K. HUNTINGTON, Assoc.R.S.M. (Vice-President), wrote that on page 66 the "breaking down of apparent β crystals" in 2.75 per cent. alloy was really something quite different, namely, the separation of an insoluble iron constituent, and not separation of the γ constituent.

Professor Carpenter's last paragraph on page 73 was not in agreement with statements in his paper read in January 1911,* wherein it was inferred that brittleness in old brass wire was due to $\beta \rightarrow \alpha + \gamma$ inversion taking place at ordinary temperatures over a long time.

He (Professor Huntington) also wished to point out, with reference to manganese mentioned by Professor Carpenter on page 68, that, according to Wologdine,† manganese formed a compound with copper, and that there was an eutectic of this compound with manganese.

* *Journal of the Institute of Metals*, No. 1, 1911, vol. v. p. 127.

† *Revue de Metallurgie*, No. 4, 1907, vol. xxv.

Mr. F. JOHNSON, M.Sc. (Birmingham), wrote that he regarded the work of Professor Carpenter as having peculiar value apart altogether from its original object in clearing up obscure points relating to the apparent β phase. For instance, the author had shown very clearly the solubility of lead, bismuth, and iron (in small quantities) in the β phase. There was thus explained, as the writer had formerly predicted, the reason why alloys of the Muntz metal type would roll hot when they contained those impurities, whereas alloys consisting entirely of the α phase, such as the 70/30 alloy, were extremely sensitive to their influence, the latter alloys having to be made from very pure copper and zinc if they were intended for hot rolling. The point to be remembered was that many kinds of Muntz metal consisted almost entirely of β at the rolling temperature. In that connection the author's experiments served to show the complexity of the relations existing between metals and impurities. What was regarded as a beneficial impurity in some metals was quite fatal in others. As he (Mr. Johnson) had shown elsewhere, arsenic and antimony, although beneficial up to a certain point in copper, exerted together a most deleterious action in brass. Almost the reverse of that held in the case of bismuth, and by demonstrating the solubility of the latter in the β phase, and the precipitation of γ by the addition of antimony, the author's results went far towards rendering a satisfactory explanation of those phenomena.

The writer did not entirely agree with the deduction drawn by Professor Carpenter from his diffusion experiments with pure β and the vanadium alloy containing free γ . As Mr. Hudson had pointed out at the meeting, vanadium itself might diffuse into the β alloy, and thus exert an influence at the surface similar to that which it had exerted in the mass of the alloy to which it had been added. It would be interesting to test the β alloy for vanadium. Moreover, the diffusion of zinc had by no means reached a state of equilibrium in the author's experiment, and the superficial layer of the β alloy, which was examined by the author at the end of the experiment, was probably richer in zinc than the subjacent portions—so rich in fact, as to show the presence of free γ . Had sufficient time been allowed for the attainment of equilibrium, doubtless the author's contention on p. 57 ("The structural resolution of the pure copper-zinc β constituent into $\alpha + \gamma$ ") would have held good. In other words, "a mean excess of 0.5 per cent. γ over the two alloys if diffusion occurred" might not account for the presence of structurally free γ in an alloy of eutectoid composition, but a surface layer of such an alloy could be made to contain much more than 0.5 per cent. excess γ under conditions of incomplete equilibrium, particularly as the points of contact were mainly γ , owing to it standing out in relief. There seemed to be some controversy over the identity of the phase coexisting with γ in some of the specimens. The author identified it as α ; others contended that it was β . Could the author persuade some of the alloys to submit to some form of mechanical working? If the phase were α it would reveal twinning after annealing; if β , no twinning would occur.

Referring to the results of Professor Carpenter's experiments on the effect of added metals on the structure of β , he (Mr. Johnson) would be glad to know if the proof were absolutely conclusive that the light-blue crystals in Plate XIV. Fig. 4 were really bismuth. Was there a distinct difference in colour between these crystals and pure γ ? Only visual examination could reveal such a difference, and it also seemed quite possible that if, as the author stated, free bismuth could separate from the β constituent, why not free Cu_3Sb or Cu_4Sn , in the case of the antimony and tin alloys? The writer had no intention of suggesting that such was the case, but he would be glad if Professor Carpenter would state clearly his proof of the identity of the light-blue crystals as pure γ .

The writer objected to the use of the term " α -tin cuprite" on page 65. He considered that the use of mineralogical terms for metallographical entities was inadvisable, especially so as their use in the metallography of iron and steel had led to considerable opposition. He thought that to describe the constituent as the α phase of the copper-tin alloys was clearer and more in accordance with modern metallographic nomenclature.

Professor CARPENTER, in reply to the communications, wrote that Professor Huntington appeared to question the author's statement (page 68) that "manganese and copper are soluble in all proportions" by quoting the research of Wologdine, according to which manganese formed a compound with copper, and this compound formed a eutectic with excess of manganese. Professor Huntington was evidently unaware that Wologdine's work on the copper-manganese equilibrium was now discredited. It was shown by Zemozuzny, Urasow, and Rykowskow that carbides were formed in Wologdine's alloys owing to the fact that he melted his metals under charcoal. He was, therefore, not dealing with copper-manganese alloys, but with ternary mixtures. The most probable form of the equilibrium diagram was that given in Guertler's *Metallographie*, page 93, which is based on the concordant results of the above-mentioned authors and those of Sahmen. According to these, there is no break in the field of solubility below the liquidus from one side of the diagram to the other.

Mr. F. Johnson questioned the validity of the author's deductions as to the resolution of the pure β constituent by means of the "nucleus" action of the 0.95 per cent. vanadium alloys. His criticism appeared to be due to an imperfect study of the author's statements. Thus he said: "... The diffusion of zinc had by no means reached a state of equilibrium" . . . and "had sufficient time been allowed for the attainment of equilibrium doubtless the author's contention . . . would have held good." The author would venture to direct Mr. Johnson's attention to the following sentences quoted from page 56 of his paper: "Once the action had been started the vanadium alloy was withdrawn, and the annealing of the apparent β continued alone. This extended ultimately over ten weeks." In the face of such precautions to ensure equilibrium and complete diffusion, it was impossible for Mr. Johnson to maintain his

contention that sufficient time for the attainment of equilibrium had not been allowed. So far as the author was aware, no constituent of any other metallic mixture had ever been so drastically annealed.

The crystals of free bismuth (Plate XIV. Fig. 4) commented on by Mr. Johnson were not light blue, but metallic grey in colour. His suggestion that from the antimony and tin alloys compounds such as Cu_3Sb or Cu_4Sn —the latter is, strictly speaking, not a compound but a solid solution whose composition varies within certain limits—could separate was quite possibly correct, but each of these mixtures was a ternary and not a binary system, and the exact composition of the separating constituent could only be determined by experiment.

Mr. Johnson objected to the author's use of the term "*a*-tin cuprite," and that of "mineralogical terms for metallographical entities . . . especially as their use in the metallography of iron and steel had led to considerable opposition." It was easier to dispute over nomenclature than anything else, and nothing was less worth it, and therefore the author would content himself by saying that Mr. Johnson's references to the metallography of iron and steel appeared to have their origin in an important misapprehension of the position. The terms ferrite, cementite, and pearlite—all of them mineralogical in their origin—were universally accepted and used at the present day. Opposition had never been taken to them, but to other "ites," such as troostite and sorbite, not because they were mineralogical, but because there were reasons for doubting their existence as constituents.

In using the expression "*a*-tin cuprite," denoting the *a* copper-tin solid solution, the author had followed Guertler (*Metallographie*, pp. 667 and 668). The advantage of this nomenclature was that it lent itself to such classifications as *a* zinc cuprite, *a* aluminium cuprite, *a* antimony cuprite, &c. &c., in referring to these corresponding *a* constituents.

ON THE ANNEALING OF COINAGE ALLOYS.*

BY THOS. KIRKE ROSE, D.Sc.

THE methods used in coinage are well known, and need not be described at length here. The cast bars are gradually reduced in thickness by cold rolling, becoming harder with each passage through the rolls. At the Royal Mint, gold is not annealed during rolling, but silver, bronze, and nickel are annealed once. In the United States Mints, silver is not annealed at this stage. Blanks of all kinds are annealed before they are passed to the coining press.

Little has been published as to the temperature and time required for annealing in mints,† and the present paper describes experiments made to determine them. Some pure metals were also examined, with the result that further light has been thrown on the change from the hard to the soft state of metals. This has already been dealt with exhaustively by Dr. G. T. Beilby in his May Lecture last year before this Institute,‡ when he gave incidentally some data on the annealing of gold, silver, and copper.

In a research made in 1911, § M. Matweeff hardened certain metals and alloys by cold hammering, and annealed them for five minutes at various temperatures. He measured the hardness by means of M. Le Gris' modification of Brinell's method. M. Matweeff examined zinc, aluminium, copper, nickel, cartridge-brass, and aluminium-bronze. His conclusions were as follows:—

1. Pure metals hardened by hammering do not begin to lose their hardness on annealing until a definite temperature

* Read at Autumn General Meeting, London, September 25, 1912.

† For the temperature formerly employed in annealing blanks in the Royal Mint, see Hill and Roberts-Austen, "Twenty-sixth Annual Report of the Mint," 1895, p. 129. It varied considerably, but was usually between 600° and 700° C.

‡ G. T. Beilby, "The Hard and Soft States in Metals," *Journal of the Institute of Metals*, No. 2, 1911, vol. vi. pp. 5 *et seq.*; *Philosophical Magazine*, August 1904, p. 273; *Proceedings of the Royal Society*, 1907, vol. 79A, p. 463.

§ M. Matweeff, "Notes sur le Recuit des Metaux," *Revue de Métallurgie*, September 1911, p. 708.

is reached: 100° for zinc, 300° for copper and silver, 350° for aluminium.

2. The complete change of hardness occurs abruptly within a limited range of temperature.

3. Alloys begin to lose their hardness at a temperature different from that of the predominant metal, and annealing extends over a greater range of temperature than that required for pure metals.

I have approximately confirmed M. Matweeff's results when the metals and alloys are annealed for five minutes as in his experiments, but if any other length of time is used the results are different.

The method which I adopted for determining the effects of annealing was to measure the hardness of the metals and alloys by means of the scleroscope. I also examined the change of density and the extent of recrystallization in certain cases.

The scleroscope is fully described elsewhere,* and need not be discussed in detail here. It consists of a small tup-hammer, which is let fall on the surface of the metal to be examined, and the height of the rebound observed. It was used instead of a Brinell machine on account of its convenience in dealing with small specimens, the minimum thickness required being only 0.03 inch (0.76 millimetre) with the scleroscope. As the result of tests on blanks by striking them between dies, it was found that the degree of perfection of the coins depends on the hardness of the blanks as measured by the scleroscope. When a blank was comparatively hard, according to the reading of the scleroscope, the coin struck from it was less perfect, or in mint language, less "up," than that made from a blank which was softer by a few points on the scale, as I have shown elsewhere.†

As comparatively soft metals were to be measured, the "magnifier hammer" was used throughout. A few tests were made with the "universal hammer," and the relation found to agree with that given by the makers of the instrument. To

* See *The American Machinist*, 30th November 1907; *Cassier's Magazine*, September 1908; also paper read by Shore, the inventor of the instrument, before the Leicester Association of Engineers, 7th November 1908. See also Turner, *Journal of the Iron and Steel Institute*, No. I. 1909, vol. lxxix, p. 426.

† Memorandum on "The Hardness of Coins," Annual Report of the Mint, 1911.

translate the hardness numbers given in this paper into those of the universal hammer, they must be reduced in the proportion of about 7 to 4. To obtain the corresponding numbers in the Brinell scale of hardness, approximately, it is said to be sufficient to multiply by six the universal hammer numbers, but I could not find any close obvious relation between the numbers which I obtained and those given by M. Matweeff for zinc, copper, &c. Apparently M. Matweeff's hammered specimens were very far from being at maximum hardness, but the hardness numbers of his annealed specimens, if converted as usual, were similar to those which I found. The main point in such work is less to establish absolute numbers denoting hardness than to obtain relatively correct numbers. On the scale used in this paper, the hardness number of lead is 1.5, that of soft annealed copper about 13, and that of hardened die steel about 175.

In finding the hardness number of a specimen, ten readings were usually made and the mean taken. Sometimes a larger number of readings were taken, but the means of any successive groups of ten readings were not found to vary appreciably. Single tests at different parts of the same specimen often varied two or three points on hardened sheets. The specimens were usually prepared by casting into bars either $\frac{1}{4}$ inch or $\frac{1}{2}$ inch thick and rolling down to $\frac{1}{16}$ th inch thick. In most cases this method gave the maximum hardness which it was possible to attain. Certain cases are noted in which the specimens used were not at maximum hardness. Some larger specimens were also examined, as noted below, with the view of determining the effect of the dimensions of pieces of metal on the results of annealing.

The annealing at 100° and at lower temperatures was in water or in oil. In some of the experiments between 100° and 250° the specimens were heated in oil or glycerine, and in other cases in air. In some experiments at higher temperatures the medium was steam, but in all cases above 300° an electric heater was used, the specimens bound in a thermocouple, with the aid of some platinum wire, being placed in a platinum crucible, packed with charcoal powder to exclude the air. Slight oxidation often took place, and it was, of

course, necessary to remove the oxides by filing before measuring the hardness. No differences in hardness were observed to be due to a difference in the medium. Heating in oil, steam, air, or charcoal powder appeared to have the same effects.

The following tables and corresponding curves give the main results in softening, due to the annealing of coinage alloys:—

Coinage Bronze.

Copper, 95; tin, 4; zinc, 1. Maximum hardness obtainable, 70. Hardness of cast bar, 15·5.

TABLE I.—*Experiments on Penny Blanks (thickness 1·4 millimetre).*

Temperature of Annealing, Degrees Centigrade.	Duration of Heating.	Hardness.
Before annealing	61
100	192 hours	61
200	168 "	56
380	1 "	40
400	1 "	26
420	3 "	25·5
470	$\frac{1}{2}$ "	21
590	4 "	19
860	5 "	17
" (farthing blank) . . .	5 "	15·5

The results given in the table are shown in the form of a curve in Fig. 1.

In order to determine the effects of initial hardness on the results of annealing, the following experiments were made:—

TABLE II.

	Tempera- ture, Degrees Centigrade.	Time.	Hardness.	
			Before.	After.
Penny blanks (thickness 1·4 millimetre) . . . }	200	168 hours	60	55
Penny blanks	"	" "	58	53·5
Farthing blanks (thick- ness 1 millimetre) . . }	"	" "	65	59
Farthing blanks . . .	"	" "	67	61
Penny blank	470	$\frac{1}{2}$ "	60	21·3
" "	"	" "	36	21·7

The penny blank last mentioned had previously been partially annealed.

It is clear from these results that at 200° , when the softening is only just perceptible, the harder specimen remains harder after annealing, but when annealing at 470° is applied, it does not matter how hard the specimen may be before it is heated, the result is the same.

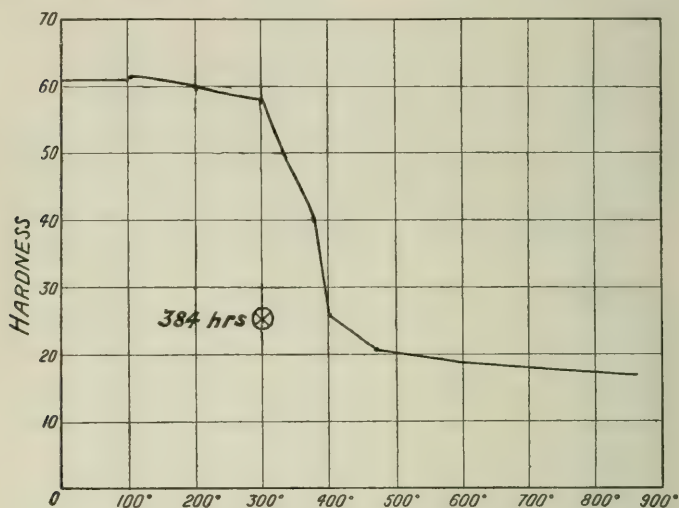


FIG. 1.—Coinage Bronze. See Table I.

It appeared probable on *a priori* grounds that if time enough were allowed, complete softening would take place at the lowest temperature at which a tendency to soften could be detected. In order to test this, the following experiments were made on halfpenny blanks of hardness 65 :—

Temperature of Annealing, Degrees Centigrade.	Time.	Hardness.
Before annealing	65
300	$\frac{1}{2}$ hour	62
290-310	70 "	45
" "	384 "	25

The conclusion is that at 300° softening would be complete in course of time. It also appears that the softening begins

at a comparatively rapid rate and gradually becomes slower and slower, so that it would be difficult to predict when equilibrium would be established. This observation applies generally to all cases of annealing examined in this investigation.

The following experiments were made to determine the results of annealing for a very short time. The specimens, with a thermocouple bound round them, were heated in charcoal-powder, and quenched as soon as they reached the desired temperature. The total time of heating in each case was about ten minutes, and in each case the last 10° increase of temperature occupied about one minute.

TABLE III.

	Temperature, Degrees Centigrade.	Hardness.	
		Before.	After.
Penny blank (thickness 1·4 millimetre)	400	64	56
" " " " " "	420	64	53
Halfpenny blank (thickness 1·24 millimetre)	440	67	32·5
Farthing blank (thickness 1 millimetre)	470	65	30
Halfpenny blank	480	68	28
" " " " " "	500	65	26·5
" " " " " "	520	64	26
" " " " " "	540	64	24·5
" " " " " "	570	64	22·5
" " " " " "	610	63	20
" " " " " "	620	65	19·5

The effect of the dimensions of pieces of coinage bronze on the temperature of annealing was examined, as follows:—

1. A halfpenny blank and a piece of bronze fillet rolled to the gauge at which it is annealed in the ordinary course at the Mint were heated rapidly and quenched as soon as the temperature reached 600° .

	Hardness after Annealing.
Halfpenny blank, thickness 1·24 millimetre . . .	21
Fillet " 2·4 " . . .	23

2. A penny blank and a similar piece of bronze fillet were heated at 470° for half an hour.

	Hardness after Annealing.
Penny blank, thickness 1·4 millimetre . . .	21·5
Fillet " 2·4 " . . .	25·5

The difference in hardness of the annealed pieces, though appreciable, are seen to be small. Similar results were obtained by comparing thin and thick pieces of standard silver, 925 fine.

The conclusions to be drawn as to the annealing of coinage bronze are that softening begins at about 200° , but is very slight below about 380° if only a limited time is allowed. Annealing is practically complete at about 470° in half an hour, or at about 600° (near the lowest limit of redness) in a minute or two. It is nearly complete at 300° in 384 hours. The smaller pieces of metal are annealed more readily than larger pieces.

Silver-Copper Alloys.

TABLE IV.

Temperature, Degrees Centi- grade.	Time.	Hardness.					
		No. 1. Ag 924, Cu 76.	No. 2. Ag 915.5, Cu 84.5.	No. 3. Ag 899.5, Cu 100.5.	No. 4. Ag 836, Cu 164.	No. 5. Ag 799, Cu 201.	No. 6. Ag 720, Cu 280.
Before an- nealing	...	56	71	73	75	76	77
230	1 hour	53	69	71	74	76	...
300	$\frac{1}{2}$ hour	51	...	67	...	71	73
350	"	43	60	59	65	68	70
400	"	35	49	52	54	59	...
425	"	60
460	"	31	42	43	49	51	...
500	"	29.5	36	40	46	47.5	50
550	"	23.5	30	33	37	39	...
600	"	...	24	27	32	37.5	37
650	"	21	24	25.5	29.5	37	...
700	"	28.5
700-720	3 hours	20
740	$\frac{1}{2}$ hour	...	23	23.5	28.5	31	...
Cast speci- men	...	24

The results given in the table are shown in the curves in Fig. 2. The alloys, silver 600, copper 400, and silver 400, copper 600 were also studied, and their behaviour on annealing found to resemble closely those of the alloy silver 800, copper 200.

The alloy, silver 925, copper 75, was a piece of gauged fillet which had been annealed when 2.73 millimetres thick

(its hardness being thus reduced from 66 to 37), and its hardness raised to 56 by subsequent rolling to 1·70 millimetres thick. The maximum hardness of this alloy is about 68. The other alloys were at about maximum hardness. This difference has caused curve 1 in Fig. 2 to be lower than would otherwise be the case at the lower temperatures.

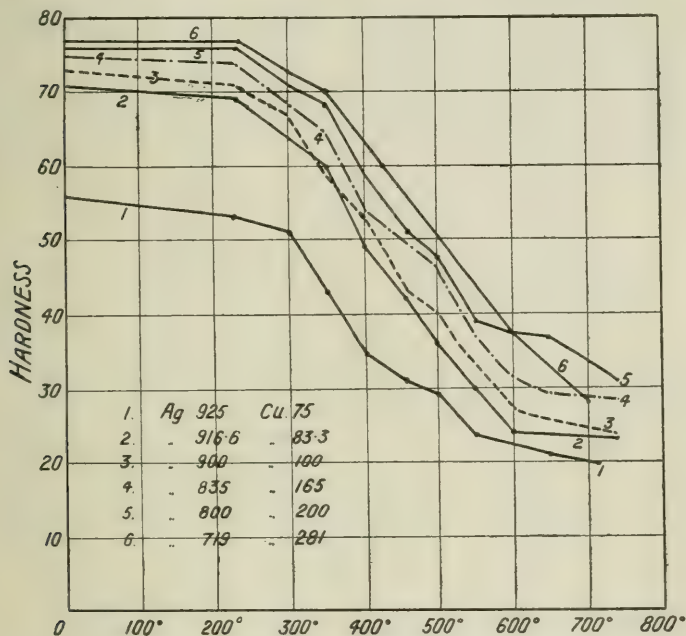


FIG. 2.—Silver-Copper Alloys.

The effect of time was tested at 300°, which is not much above the temperature at which softening begins to be perceptible, with the following results:—

Time at 300° C.	No. 1. Ag 924, Cu 76.	No. 3. Ag 899·5, Cu 100·5.	No. 6. Ag 720, Cu 280.
Before annealing	56	73	77
$\frac{1}{2}$ hour	51	67	73
70 "	31·5	43·5	58·5
384 "	24·5	27·5	37

As in the case of bronze, the results indicate that the temperature is high enough to effect complete softening if more time had been allowed.

Softening is seen to begin in the alloys of higher standard at about 230° , and in those of lower standard at a somewhat higher temperature.

Annealing is practically complete in half an hour in the 925 alloy at about 550° , and requires a gradual increase of temperature as the proportion of copper increases.

The result of annealing for a very short time are as follows, the experiments being carried out as in the case of bronze:—

TABLE V.

Temperature, Degrees Centigrade.	Hardness.			
	Ag 924, Cu 76.	Ag 899.5, Cu 100.5.	Ag 836, Cu 164.	Ag 799, Cu 201.
Before annealing	56	73	75	76
320	56	73	...	76
350	51	72.5	73	75.5
400	39	68.5
450	34	61.5	56.5	63.5
500	[27.5]	58
550	25	45	45.5	51
600	22	42.5
700	21.5	31.5

Softening is thus practically complete in a minute or two in the 925 alloy at about 600° , and in the 800 alloy at somewhat above 700° .

Gold-Copper Alloys.

The maximum hardness attained with standard gold—Au 916.6, Cu 83.3—was 76. The maximum hardness of the 900 alloy was not determined.

The results given in Table VI. are shown in the curves in Fig. 3.

TABLE VI.

Temperature, Degrees Centigrade.	Time.	Hardness.	
		Au 916·6, Cu 83·3.	Au 900, Cu 100.
Before annealing	65	69
230	1 hour	65	69
290	"	63	...
300	$\frac{1}{2}$ "	60	69
350	"	58	62
400	"	41	44
460	"	32	39
500	"	30·5	35·5
550	"	30	34
720	3 hours	...	29
740	$\frac{1}{2}$ hour	...	29
Cast bar	23	...

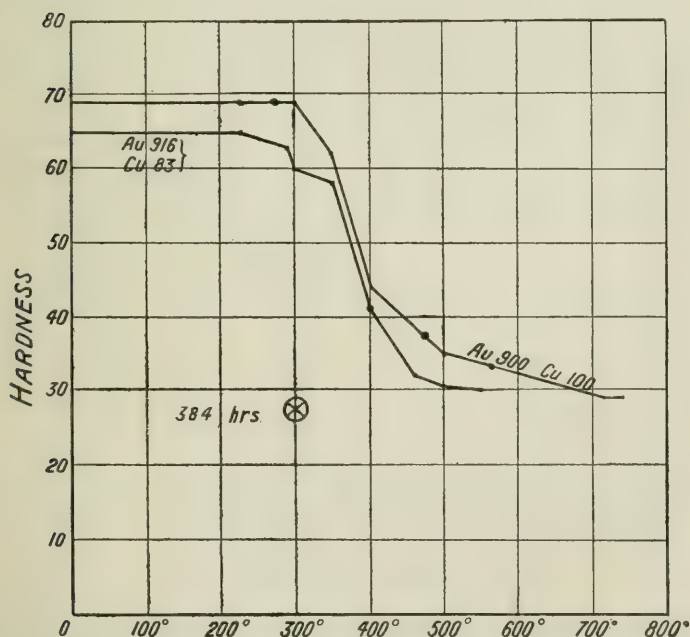


FIG. 3.—Gold-Copper Alloys.

The results of annealing for a very short time are as follows, the experiments being carried out as for bronze :—

TABLE VII.

Temperature, Degrees Centigrade.	Hardness.	
	Au 916·6, Cu 83·3.	Au 900, Cu 100.
Before annealing	65	69
320	54	64·5
350	63
405	50	51
450	37
510	32·5	...
550	35
600	28	31
700	23	31
800	22	...

The effects of time are seen to be very little at temperatures above 500°, although very strongly marked at 300°, the lowest temperature at which softening was observed to take place. At this temperature the alloys were annealed for various times with the following results :—

Time of Heating at 300° C.	Hardness.	
	Gold 916·6, Copper 83·3	Gold 900, Copper 100.
Before annealing	65	69
$\frac{1}{2}$ hour	60	69
70 „	35	42·5
384 „	28·5	28

Softening is seen to be nearly complete in these alloys in 384 hours.

Nickel-Copper Alloys.

Of these alloys, the nickel 25 per cent. is that which is now invariably used for coinage. The reason for the curious

TABLE VIII.

Temperature, Degrees Centigrade.	Time.	Hardness.			
		Ni 20, Cu 80.	Ni 25, Cu 75.	Ni 30, Cu 70.	Ni 50, Cu 50.
Before annealing	64	75	77	87
300	$\frac{1}{2}$ hour	...	66	65	...
290-310	70 hours	58	62	60.5	86
" "	384 "	51	52.5
410	$\frac{1}{2}$ hour	55.5	79.5
425	"	...	62.5	59	...
500	"	40	60.5	32	76
550	"	24	44	26	55
600	"	...	31	23.5	...
650	"	21.5	26	...	37
700	"	...	23.5	21.5	...
800	"	...	23.5	21.5	...
900	"	17.5	31.5

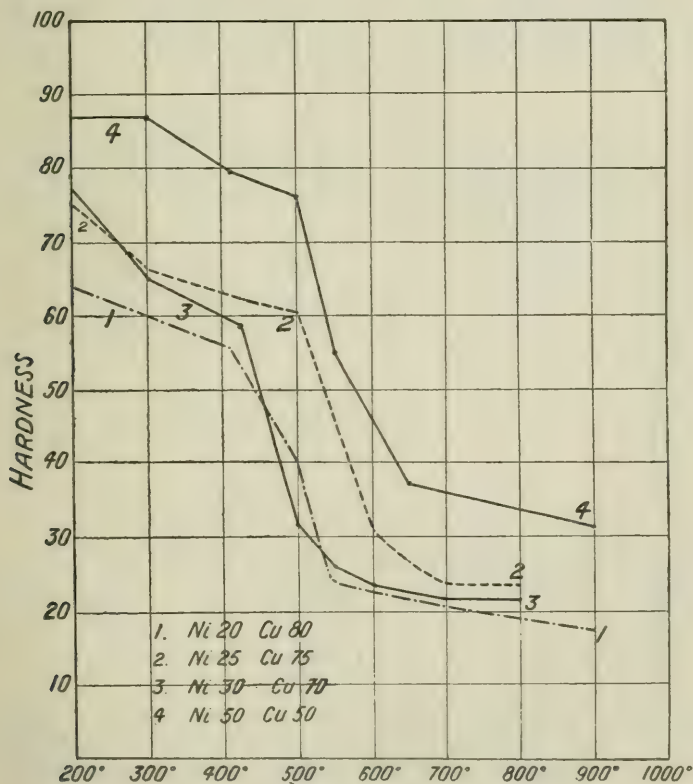


FIG. 4.—Nickel-Copper Alloys.

behaviour of the 30 per cent. alloy was not discovered. There is a general similarity between the results on annealing of the 25 per cent. alloy and that of pure nickel, which are given on p. 101. The effect of time at 300° is not great.

The general conclusions on the coinage alloys are given at the end of the paper.

PURE METALS.

The following experiments were made on pure metals:—

Gold.

1000 fine: cast in ingot 6·5 millimetres thick; hardness, 5; rolled down to 1 millimetre thick; hardness, 35.

TABLE IX.

Temperature of Annealing, Degrees Centigrade.	Duration of Heating.	Hardness.
Not annealed	35
100	1 hour	35
104	1 "	33
108	2 "	26·5
115	1 "	28
120	$\frac{1}{2}$ "	27
125	1 "	14
128	3 "	6·6
150	1 "	5·7
230	1 "	5·6
300	$\frac{1}{2}$ "	5·4
350	$\frac{1}{2}$ "	5·3
400	$\frac{1}{2}$ "	5·0
800	2 "	4·5
The above results are shown in one of the curves in Fig. 5.		
80	100 hours	14
100	100 "	7·2
105	120 "	6·5
120	24 "	6·35
140	168 "	6
240	168 "	6

In the following experiments the gold was heated in oil or glycerine from the cold in from four to nine minutes,

and quenched as soon as the temperatures given were reached:—

Temperature.	Hardness.
150°	25·6
175°	16·5
200°	6·6
250°	6·4
320°	6·2
400°	6·0

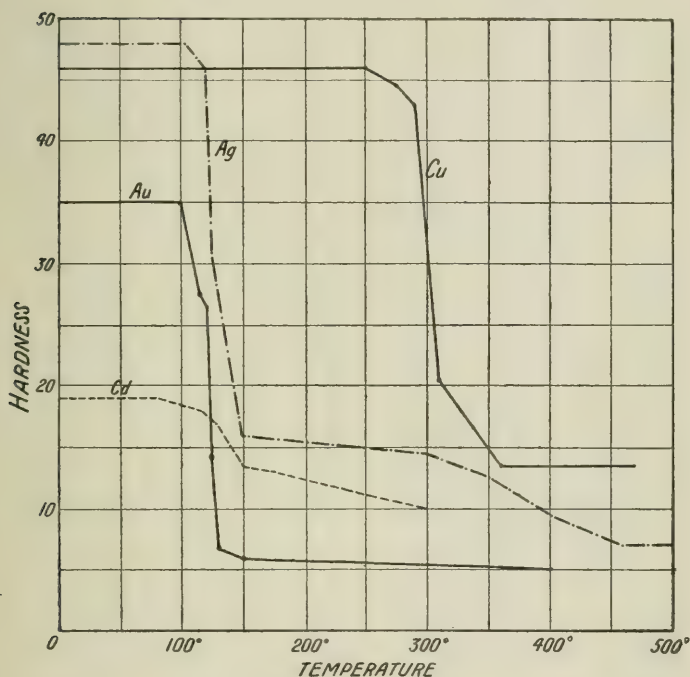


FIG. 5.—Pure Metals.

Silver.

1000 fine: cast in ingot 12·5 millimetres thick; hardness, 7; rolled down to 1·27 millimetres thick; hardness, 48.

Copper.

Pure electrolytic, 100·0 per cent.: hardness of casting before rolling, 7; rolled down to 1·15 millimetres thick; hardness, 46; maximum hardness, over 50.

SILVER. TABLE X.

Temperature of Annealing, Degrees Centigrade.	Duration of Heating.	Hardness.
Not annealed	48
100	1 hour	48
104	1 "	48
115	1 "	45
120	$\frac{1}{2}$ "	46
125	$\frac{1}{2}$ "	31
128	$\frac{3}{4}$ "	24
150	1 "	16
230	1 "	14.5
300	$\frac{1}{2}$ "	14.5
350	$\frac{1}{2}$ "	12.5
400	$\frac{1}{2}$ "	9.5
460	$\frac{1}{2}$ "	7
500	$\frac{1}{2}$ "	7

The above results are shown in a curve in Fig. 5.

400 } 500 }	Quenched as soon as temperature was reached	{ 11.5 8
80	100 hours	23.5
100	100 "	20.2
105	120 "	16.5
120	24 "	20
140	144 "	15.5

COPPER. TABLE XI.

Temperature of Annealing, Degrees Centigrade.	Duration of Heating.	Hardness.
Not annealed	46
150	144 hours	46
250	1 "	46
275	1 "	44.5
290	1 "	43
290-310	70 "	12.5
310	1 "	20.5
360	2 "	13.5

The above results are shown in a curve in Fig. 5.

360	} Quenched as soon as temperature was reached {	46
380		24
400		14
420		13
470		13

Nickel.

Pure Mond nickel (Ni 99.58 per cent.): casting 6.5 millimetres thick; rolled to 1.8 millimetres; hardness, 75.

NICKEL. TABLE XII.

Temperature of Annealing, Degrees Centigrade.	Duration of Heating.	Hardness.
Not annealed	75
128	3 hours	75
300	1 3/4 "	73
425	2 1/2 "	69
525	1 1/2 "	61
550	1 1/2 "	47
625	3 1/2 "	27.5
700	3 1/2 "	21.5
800	1 1/2 "	21
290-310	70 "	66
" "	384 "	36

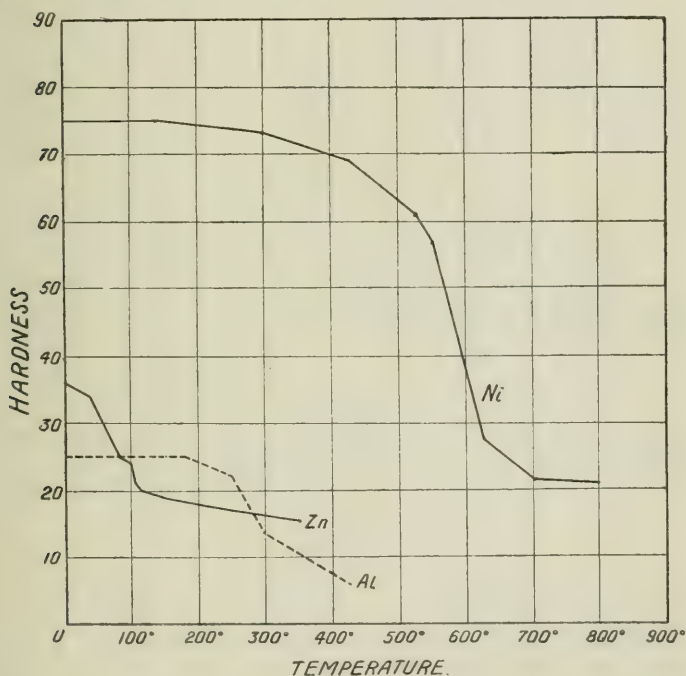


FIG. 6.—Pure Metals.

There is a general similarity between the behaviour on annealing of pure nickel and that of the alloy, nickel 25, copper 75, as given above in Table VIII. The effect of prolonged heating of nickel at 300° is greater than in the nickel-copper alloys.

Zinc.

Free from arsenic, sulphur, and phosphorus: iron, 0.005 per cent.; cast into ingot, 6.5 millimetres thick; hardness, 12.5; rolled at ordinary temperature without cracking to 1.25 millimetres thick; hardness, 36.

TABLE XIII.

Temperature of Annealing, Degrees Centigrade.	Duration of Heating.	Hardness.
Not annealed	36
41	1 hour	34
50	1 "	32
60	1 "	26
85	$\frac{1}{2}$ "	25
100	$\frac{1}{2}$ "	24
104	$\frac{1}{2}$ "	23.5
105	120 "	20
108	1 "	21
115	1 "	20
128	3 "	18.5
150	40 minutes	19
250	30 "	17
350	30 "	15.5

The effect of time in the case of zinc is seen to be comparatively slight at temperatures above 100°. The results are shown in a curve in Fig. 6.

Cadmium.

Bought as pure: cast into ingot, 6.5 millimetres thick; hardness, 10; rolled to 1.3 millimetres thick; hardness, 19.

TABLE XIV.

Temperature of Annealing, Degrees Centigrade.	Duration of Heating.	Hardness.
Not annealed	19
80	100 hours	15
100	100 "	14.7
105	120 "	12
115	1 "	18
120	24 "	12
128	3 "	17
150	40 minutes	13.5
180	30 "	13
300	30 "	10

The results are shown in a curve in Fig. 5. This metal was not analysed, and may be impure.

Aluminium.

Aluminium, 97·9 per cent.; iron, 2·1 per cent.; cast into ingot, 12·5 millimetres; hardness, 6; rolled to 1·25 millimetres; hardness, 25.

TABLE XV.

Temperature of Annealing, Degrees Centigrade.	Duration of Heating.	Hardness.
Not annealed	25
150	40 minutes	25
180	30 "	25
250	30 "	22
300	30 "	13·5
425	30 "	6
290-310	70 hours	7

These results are shown in a curve in Fig. 6.

Antimony when cast had a hardness of 30, but broke into powder at the first passage through the rolls.

Bismuth when cast had a hardness of 7, and broke up on its third passage through the rolls. Its hardness at this point appeared to be 7·5.

Tin when cast had a hardness of 4. This was raised to 6 by rolling. No annealing experiments were made.

Lead when cast had a hardness of 1·5, which was not altered by rolling. (See, however, footnote on p. 105.)

EFFECT OF TIME IN ANNEALING.

The curves given in Figs. 1 to 6 are based on the experiments made for a limited time, generally from half an hour to one hour. It was at first thought that that time was enough for equilibrium to be attained, at each temperature used both in pure metals and alloys, and the curves are, to some extent, comparable with those drawn by M. Matweeff. It was afterwards found that if a longer time had been taken—a day, a week, or longer—the curves would be quite different. For

example, if silver is annealed for 24 hours at 120° it is left harder than if it is annealed at 105° for 120 hours, but softer than if it is annealed at 128° for 3 hours, thus:—

Time.		Temperature, Degrees Centigrade.	Hardness.
120 hours	105	16.5
24	„	120	20
3	„	128	24

so that it is clear that time is of great importance as well as temperature.

If the time of annealing is short, it is possible to determine approximately the temperature at or about which a metal begins to soften. As the temperature rises, softening is hastened, until at a much higher temperature annealing is almost instantaneous. Between these upper and lower limits of annealing temperatures, the only difference is the rate at which the metal loses its hardness, the ultimate condition being the same if time enough is allowed. The determination of the upper and lower limits can only be approximate for the following reasons.

At the lowest temperature at which change occurs it would take an almost infinite time before the amount changed would be perceptible. On the other hand, the change would presumably take place more and more quickly as the temperature rises, up to the melting point. The practical limits of temperature might be taken as those at which say 95 per cent. of the change takes place in a few days and one minute respectively. For gold, these appear to be about 80° and 200° ; for silver, 80° and 500° ; for copper, perhaps 275° and 400° .

Such a change as that described above agrees with Dr. Beilby's conception of the hard and soft states of metals as being two separate forms or species of matter. The observed facts are also in consonance with the prevalent view that annealing is primarily the relief of strains.

It has generally been supposed that the soft state is the stable condition of all metals at ordinary temperatures, and the

hard state an unstable condition. It appeared to me probable, therefore, that all hard metals are gradually softening at the ordinary temperature. This was found to be the case with some rolled specimens of tin, cadmium, and zinc, which were again examined ninety-seven days after their hardness had been tested. The hardness of tin had fallen from 6 to 4·5 in that time, the metal becoming almost as soft as the original cast ingot. The hardness of zinc had fallen from 36 to 31, and that of cadmium from 19 to 14. These specimens had been kept at a temperature of about 15°.

In view of these facts it is not unlikely that the reason why lead cannot be hardened * at the ordinary temperature is that it undergoes a rapid change from the hard to the soft state below 15°. This could be determined by working it at low temperatures.

A further opportunity of testing the softening of metals at the ordinary temperature was afforded by the existence of the ancient gold and silver trial plates of this country which are preserved at the Mint. These plates were assayed by Sir William Roberts-Austen in 1874, and the analyses given below are quoted from his paper.†

The oldest plates are of irregular shape and thickness, and have been somewhat roughly hammered out. The fine gold plate of 1477 is in part 3·2 millimetres in thickness, but another part has been hammered out to a thickness of 0·92 millimetres, making the plate chisel-shaped in order to receive the impression of a coin. The fine gold plate of 1560 also bears the marks of the hammer, but it is of almost uniform thickness and has been flattened with much greater skill. The plates of 1605, and of all later dates, have been rolled out. The silver plates have been prepared in the same way as the gold plates of corresponding age. The hardness of some of these plates was tested by the scleroscope with the following results:—

* Ewing and Rosenhain found that lead is mechanically hardened to a small extent by severe strain (see *Philosophical Transactions of the Royal Society*, vol. 195A (1901), p. 291), but the hardening would not last very long.

† *Journal of the Chemical Society*, vol. xxvii. (1874), p. 197. Photographs of the plates are given by Roberts-Austen in *Journal of the Society of Arts*, vol. xxxii. (1884), p. 888.

TABLE XVI.

	Date of Preparation.	Composition.	Thickness in Millimetres.	Hardness.
Fine gold	1477	{ Gold, 993·5 Silver, 5·15 Copper, 1·35 }	3·2	10
" "	"	"	0·92	17
" "	1560	{ Gold, 994·3 Silver, 5·7 Copper, ... }	1·64	8
" "	1605	{ Gold, 990·3 Silver, 8·3 Copper, 1·4 }	1·02	23·2
" " (another separate portion of the 1605 plate) }	0·82	24·6
" " }	1873	Gold, 1000·0	0·78	27
" " (made in Royal Mint) }	1901	" "	0·58	29
" " " "	1912	" "	1·02	35
Standard gold	1527	{ Gold, 915·5 Silver, 78·3 Copper, 6·2 }	1·68	14·2
" "	1560	{ Gold, 913·7 Silver, 60·8 Copper, 25·7 }	1·3	20·3
" "	1660	{ Gold, 912·9 Silver, 53·3 Copper, 33·8 }	...	25·2
" "	1707	{ Gold, 917·1 Silver, 59·5 Copper, 23·4 }	0·73	24·3
" "	1728	{ Gold, 916·1 Silver, 50·4 Copper, 33·5 }	0·75	27·7
" "	1829	{ Gold, 915·3 Silver, 37·6 Copper, 46·5 }	0·97	35
" "	1912	{ Gold, 916·7 Silver, 83·3 Copper, ... }	0·7	40·3
" "	1912	{ Gold, 916·7 Silver, ... Copper, 83·3 }	1	74
Standard silver	1477	{ Silver, 923·5 Copper, 76·5 }	5	24
" "	"	"	2·5	34·6
" "	1560	{ Silver, 930·2 Copper, 69·8 }	1·75	29·4
" "	1688	{ Silver, 922 Copper, 78 }	...	38·2
" "	1873	{ Silver, 924·96 Copper, 75·04 }	1·95	61·3
" "	1912	{ Silver, 925 Copper, 75 }	1	68

There is no certainty that the plates of 1873 have softened perceptibly as yet. There is also no certainty that the ancient trial plates were at maximum hardness when they were produced, but it is clear that they must have been harder when made than they are now. This applies both to the so-called fine gold and to the standard alloys of gold-silver and of silver-copper. The presence of copper, and to a less extent of silver, in the fine gold makes it harder. It is also clear that 400 years have not been enough to complete the softening of either fine gold or standard silver, since the thicker parts of these plates are softer than the thinner parts, which could not have been far below the maximum hardness when they were new.

It is, however, probable that gold and the alloys, gold-silver and silver-copper, as well as tin, zinc, and cadmium, soften gradually at 15° , and no lower limit of temperature can as yet be assigned to this change, unless it is the absolute zero.

RECRYSTALLIZATION ON ANNEALING.

It is well known that annealing hardened metal causes recrystallization, but it is usually assumed to be a gradual process due to long-continued heating. As softening was found to be often instantaneous, however, it appeared necessary to determine how far softening was accompanied by recrystallization. According to Dr. Beilby's theory that rolled metals owe their hardness to amorphous particles, it might be expected that the two phenomena would be simultaneous. Against this is to be set the observation made in 1907 that the crystalline structure in gold is not developed when it is heated for an hour at temperatures below about 230° .*

On etching the specimens of gold sheet in warm dilute aqua regia, it appeared that the distorted lamellæ (Fig. 7, Plate XX.), which showed the remains of the original primary crystalline grains, were broken up with the formation of differently oriented crystals as soon as softening took place. The specimens heated at 80° for 100 hours, with a hardness of 14, as

* *Proceedings of the Royal Society*, 1907, vol. 79A, p. 467.

against 35 for the rolled plate, already show very distinct traces of the new crystalline aggregates, although the outlines of the lamellæ still remain intact (Fig. 11, Plate XXI.). In gold heated at 100° for 100 hours, hardness 7.2, the lamellæ are still obscurely visible, but recrystallization is not far from complete (Fig. 12, Plate XXI.). Gold heated at 150° for a moment shows no certain signs of recrystallization, its hardness being 25.6 (Fig. 8, Plate XX.). In that heated at 175° for a moment (total time of heating, beginning in cold glycerine, $4\frac{1}{2}$ minutes), hardness 16.5, the recrystallization, though visible (Fig. 9, Plate XX.), is less distinct than in gold heated at 80° for 100 hours, hardness 14 (Fig. 11, Plate XXI.). Gold heated to 200° for a moment has a hardness of 6.6, and here recrystallization is almost complete, although in this case the total time of heating, starting with the cold specimen in cold oil, was only seven minutes (Fig. 10, Plate XX.). In all these specimens the new crystals are somewhat ragged in outline, and are quite unlike the polygonal crystals which characterize annealed metals. A specimen heated at 125° for an hour still retained a hardness of 14, and in this specimen (Fig. 13, Plate XXI.) the original lamellæ have remained visible, the new crystalline growths being similar to, though somewhat less marked than, those in the specimen heated at 80° for 100 hours.

Most of the gold specimens were etched without being polished or treated in any way after annealing. Others were polished and etched without altering the results. The recrystallization can readily be seen by unassisted vision.

In the specimens referred to above, whether the heating was for a long or a short time, whenever the hardness is low, recrystallization has taken place. On the other hand, when the hardness is high, recrystallization has not taken place. The only exception is in two specimens of hardness 14, differently prepared. In one of these, heated for a long time, the recrystallization has advanced further than in the other, which was heated for a short time (Figs. 11 and 13, Plate XXI.).

The change in hardness and recrystallization are thus proved to take place almost simultaneously in the case of

gold, with a slight lag in the visible crystallization, however, especially if the specimen is heated for a short time only.

The difference between Figs. 9 and 10, Plate XX., is particularly striking, considering that the difference in treatment of the two specimens was merely the raising of the temperature from 175° to 200° , an operation which occupied only about two minutes. The rapidity with which crystals of a millimetre in length have been formed in the specimen photographed in Fig. 10, Plate XX., contrasts strongly with the leisurely procedure which is often pictured as taking place, and quite precludes the possibility that this particular growth has anything to do with diffusion or solution.

I have spoken above of "complete crystallization," but that merely refers to the fact that the space is covered with new crystals. I do not wish to be understood to say that the change has come to an end, or all strains removed, or that equilibrium is attained. This is far from being the case.

It will be observed that the abrupt fall in the hardness of the pure metals shown in the curves in Fig. 5 is followed by a further gradual fall, which is particularly marked in the case of silver, but is perceptible in gold. After the hardness of fine gold has fallen rapidly from 35 to 6 or 7, a further fall to 4.5 takes place very slowly, and this is accompanied by a gradual growth in size of the crystals, which become bounded by straight lines, and are frequently twinned. In Fig. 14, Plate XXI., a photograph is reproduced of fine gold, which has been annealed at 800° for two hours, and has a hardness of 4.5. The crystals in this specimen are 2 or 3 millimetres in length. It appears that such crystals must be formed by the time that the metal attains its minimum hardness and annealing can be said to be really complete. The formation of these crystals is too rapid to be due to diffusion.

Portions of the fine gold trial plates made in 1560 and 1605 were also examined under the microscope. The structure of the hammered plate of 1560, hardness 8, etched without being polished, is shown in Fig. 15, Plate XXII. There are no traces left of the original grains distorted by hammering. The whole surface is occupied by minute crystals.

many of which are bounded by straight lines. The largest crystals are about 0.3 millimetres in length, or less than the size of the crystals formed in fine gold heated at 80° for 100 hours, which are themselves smaller than those formed at higher temperatures even in a few moments.*

It would be useless to examine the structure of ancient gold coins, as there is evidence that these were struck hot, and were therefore self-annealed at the time of manufacture.

The same simultaneous action as that observed in gold also takes place in cadmium. When heated at 80° for 120 hours, and also at 120° for 24 hours, the hardness being reduced from 19 to 15 and 12 respectively, complete recrystallization has taken place. When heated at 128° for 3 hours, the hardness is reduced from 19 to 17, and no recrystallization can be detected.

Zinc softened at 120° had also recrystallized, but copper heated at 150° , without being softened, showed no signs of recrystallization.

Similarly in standard gold (gold 916.6, copper 83.3) no recrystallization had taken place in the specimen heated at 290° for an hour (Fig. 16, Plate XXII.), when the hardness had been reduced from 65 to 63, but when heated momentarily to 800° , the hardness was reduced to 22 and the alloy is recrystallized, with the formation of twinned crystals bounded by straight lines, although the total time of heating from the cold was only seventeen minutes (Fig. 17, Plate XXII.).

A piece of standard gold, after being heated at 550° for half an hour, hardness 30, and another specimen heated at 300° for three days, hardness 35, both showed the outlines of the original distorted crystals, but they were broken up into new crystalline groups as in the case of partially-annealed fine gold.

Having regard to these observations, it may be concluded that recrystallization accompanies or closely follows softening quite generally in metals and alloys, and that in tin, cadmium,

* After this paper was in print, however, a similar structure was obtained by reheating to redness an ingot of the same composition as the fine gold plate of 1560 and hammering it out while hot. The evidence from the old hammered plates is thus vitiated.

and zinc, as well as in lead, the growth of crystals at the ordinary temperature would be sufficiently rapid to be readily observable.*

SPECIFIC GRAVITY.

It is well known that the specific gravity of hardened metals is reduced by annealing. The effect of annealing pure gold at a dull red heat was found by Roberts-Austen† to be a reduction of its specific gravity by 0·0128.

The following results confirm this:—

	Hardness.	Specific Gravity.
Pure sheet gold	35	19·2965 ‡
„ „ annealed at 240° for 168 hours	6	19·2858
Reduction in specific gravity	0·0107

The specific gravity of hardened gold given above, though lower than that found by Roberts-Austen (19·4123), agrees nearly with the result 19·3056 found by Stas, and the results 19·3 to 19·34 at 17·5° compared with water at 17·5° found by G. Rose.§

The specific gravities of silver and of its alloys with copper were found to be as follows:—

	Hardness.	Specific Gravity.
Pure sheet silver	48	10·4992
„ „ annealed at 460° for half an hour	7	10·4916
Reduction of density	0·0076

* The growth of crystals in lead at 15° has been studied by Sir James Ewing and Dr. Rosenhain. *Philosophical Transactions of the Royal Society*, vol. 195A, 1901, p. 279. They also examined the recrystallization of lead, cadmium, and zinc at 200°, and tin at 150°. All these temperatures are above those at which the metals soften.

† “Eighth Annual Report of the Mint,” 1877, p. 44.

‡ The specific gravities given in this paper are at 0° compared with water at 4°.

§ *Op. cit.*, p. 42. A density of 19·32 at 17·5°/17·5° corresponds to 19·297 at 0°/4°.

|| For various determinations of the density of silver see Percy's *Silver and Gold*, p. 3.

	Specific Gravity.
Standard silver. Silver, 924; copper, 76. Rolled after annealing. Hardness, 56	10·3485
Standard silver. Heated to 700° and quenched at once. Hardness, 21	10·2890
Standard silver. Heated at 700° for three hours. Hardness, 20	10·2469
Total reduction of specific gravity	<u>0·1016</u>

Roberts-Austen observed * that standard gold was more reduced in specific gravity by annealing than pure gold, and the above results show that there is a still greater divergence in this respect between pure silver and its alloy with copper.

The main point of interest, however, is the observation that the expansion of standard silver on annealing was not completed so quickly as the softening. The specimen heated up to 700° and then quenched was in the furnace fourteen minutes, and its temperature rose 17° during the last two minutes. It is almost completely softened, but only about 60 per cent. of its total possible expansion at the temperature has taken place.

SUMMARY AND CONCLUSIONS.

In Table XVIII. a summary is given of the results obtained in the annealing of metals and alloys.

The first column of figures in Table XVIII. gives the temperatures at which the metals and alloys could be completely annealed in the course of a few days or weeks.

The second column of figures gives the lowest temperatures which can be used for ordinary annealing on a commercial scale. Large pieces of metal must be heated at slightly higher temperatures or for a longer time.

The following general conclusions may be drawn from this inquiry:—

1. Metals and alloys when hardened by rolling are in an unstable condition at ordinary temperatures, and undergo a gradual change to the soft state. As the temperature rises this change is hastened, until at temperatures considerably below their melting points metals and alloys revert from the hard to the soft state almost instantaneously.

* *Loc. cit.*

PLATE XX



FIG. 7.—Pure Gold, Rolled. Unannealed.
Hardness 35.
Magnified 11 diameters and slightly reduced.

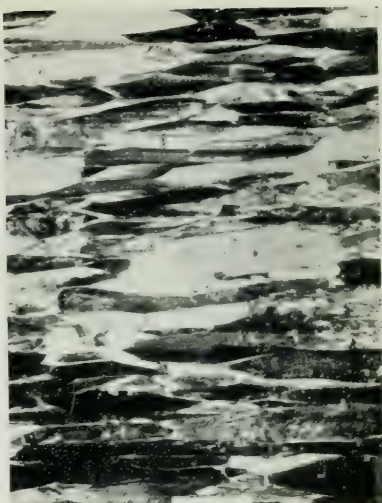


FIG. 8.—Pure Gold. Heated to 150° C.
and quenched. Hardness 25·6.
Magnified 11 diameters and slightly reduced.

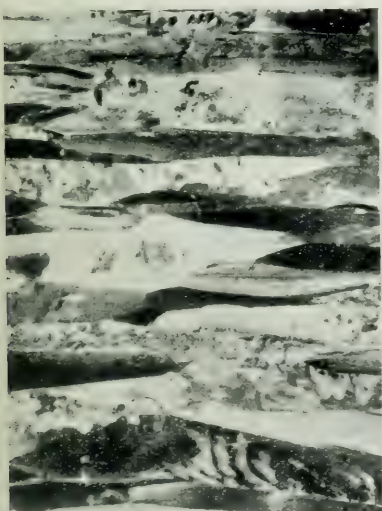


FIG. 9.—Pure Gold. Heated to 175° C.
and quenched. Hardness 16·5.
Magnified 11 diameters and slightly reduced.



FIG. 10.—Pure Gold. Heated to 200° C.
and quenched. Hardness 6·6.
Magnified 15 diameters and slightly reduced.

PLATE XXI



FIG. 11.—Pure Gold. Heated at 80° C.
for 100 hours. Hardness 14.

Magnified 11 diameters and slightly reduced.



FIG. 12.—Pure Gold. Heated at 100° C.
for 100 hours. Hardness 7·2.

Magnified 11 diameters and slightly reduced.



FIG. 13.—Pure Gold. Heated at 125° C.
for 1 hour. Hardness 14.

Magnified 7 diameters and slightly reduced.



FIG. 14.—Pure Gold. Heated at 800° C.
for 2 hours. Hardness 4·5.

Magnified 7 diameters and slightly reduced.

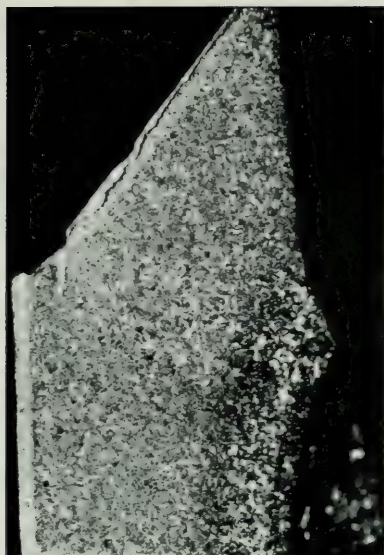


FIG. 15.—Fine Gold Trial Plate made in 1560.
Hardness 8.
Magnified 6 diameters and slightly reduced.



FIG. 16.—Standard Gold. Heated at 290° C.
for 1 hour. Hardness 63.
Magnified 4 diameters and slightly reduced.

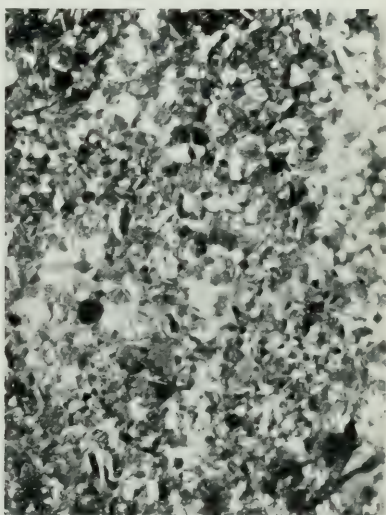


FIG. 17.—Standard Gold. Heated to 800° C.
and quenched. Hardness 22.
Magnified 15 diameters and slightly reduced.

2. The annealing action at any given temperature is most rapid at first and gradually dies away, so that a state of equilibrium is not attained in any short space of time, except perhaps at high temperatures. For example, equilibrium was apparently not attained in the gold-copper, silver-copper, or nickel-copper alloys, or in pure nickel in 16 days at 300° . At high temperatures almost the whole result is obtained instantaneously, though a little extra softness is got by prolonging the time. A few minutes at such a temperature cannot be replaced, for practical purposes, even by hours of annealing at much lower temperatures. No critical points, however, were observed.

3. When the change from the hard to the soft state takes place, recrystallization occurs almost if not quite simultaneously. The recrystallization which is visible under low magnifying powers lags behind the softening to some extent.

The characteristics of the action described in the above conclusions resemble those of the chemical change resulting from the reaction of hydrogen iodide and hydrogen dioxide studied by Harcourt and Esson,* although annealing is, of course, a physical action. It follows that it is easy to explain annealing by regarding it, following Dr. G. T. Beilby, as a change from a hard amorphous form or species of matter to a soft crystalline one.

4. Visible recrystallization and softening occur so rapidly at low temperatures, *e.g.* 200° in pure gold, as to preclude the possibility that they are dependent on diffusion. At higher temperatures polygonal crystals are produced, but their formation is also too rapid to be due to the action of diffusion.

5. In some cases (*e.g.* gold-copper alloys) alloys do not begin to soften rapidly until temperatures above that at which the predominant metal can be annealed, and the annealing extends over a greater range of temperature than that required for the pure metal. In other cases (*e.g.* nickel-copper alloys) there is no great difference in these respects between the alloys and the predominant metals.

* "On the Laws of Connection between the Conditions of a Chemical Change and its Amount,"—*Philosophical Transactions of the Royal Society*, vol. 186A, 1895, p. 817.

6. The expansion taking place on softening is far greater in alloys than in pure metals. The first softening and the breaking up of the distorted primary crystals into smaller ones with ragged edges is accompanied by a partial expansion. The remainder of the expansion accompanies a further slight softening and the formation of polygonal crystals bounded by straight lines.

TABLE XVIII.—*Summary of Results obtained in the Annealing of Metals and Alloys.*

Substance.	Lowest Temperature Observed at which Softening begins to be Perceptible. Degrees C.	Temperature at which Softening is nearly Completed. Degrees C.	
		In about Half an Hour.	In Less than a Minute.
Gold	80	130	200
Silver	80	400	500
Copper	275	360	400
Nickel	300	700	...
Zinc	15	125	...
Aluminium, containing 2 per cent. iron .	250	300-400	...
Cadmium, possibly not pure	15	150	...
Gold-copper alloys—			
Au 916·6, Cu 83·3	290	500	600
Au 900, Cu 100	300	500	600
Silver-copper alloys—			
Ag 925, Cu 75	230	550	600
Ag 916·6, Cu 83·3	230	600	...
Ag 900, Cu 100	230	600	...
Ag 835, Cu 165	(?) 230	650	...
Ag 800, Cu 200	300	700	700
Ag 719, Cu 281	300	700	...
Coinage bronze—			
Cu 95, Sn 4, Zn 1	200	470	600
Nickel-copper alloys—			
Ni 20, Cu 80	300	550	...
Ni 25, Cu 75	300	650	...
Ni 30, Cu 70	300	600	...
Ni 50, Cu 50	400	700	...

DISCUSSION.

Professor A. K. HUNTINGTON, Assoc.R.S.M. (Vice-President), said there were two points in the author's most useful and excellent paper to which he desired to draw attention. Dr. Rose stated on page 109: "It will be observed that the abrupt fall in the hardness of the pure metals, shown in the curves in Fig. 5, is followed by a further gradual fall, which is particularly marked in the case of silver, but is perceptible in gold. After the hardness of fine gold has fallen rapidly from 35 to 6 or 7, a further fall to 4.5 takes place very slowly, and this is accompanied by a gradual growth in size of the crystals, which become bounded by straight lines, and are frequently twinned." And further down he stated: "It appears that such crystals must be formed by the time that the metal attains its minimum hardness and annealing can be said to be really complete." It occurred to him that it was possible that an apparent maximum softness might be obtained by over-annealing. If one annealed at a proper temperature for a sufficient time a soft metal would be obtained without any growth of the crystalline structure; but if one went on annealing it at the temperature, then the crystals began to grow. If proper tests were made of the elastic limit, breaking strain, and elongation of the metal he thought it would be found that it had deteriorated in every way, being over-annealed. It was not, as the author suggested, that the real annealed condition of the metal had been reached, but that a condition existed due entirely to the increased size of the crystals. He thought that was a very important practical point, which was only to be arrived at by making mechanical tests for breaking, elongation, and so on. It would then be found, he thought, that the metal deteriorated all round after a certain point in the annealing was reached. On page 111 the author referred to the question of specific gravity. On the authority of Sir William Roberts-Austen and himself the author pointed out that on annealing the specific gravity was lowered. Personally, he thought it was usually recognised that if a piece of metal was worked by hammering or what not the specific gravity would at first be increased and subsequently be decreased, the increase being due to the closing-up of the interstitial spaces—the porosity due to gas or what not; the subsequent decrease in specific gravity being due to some strain set up in the metal forcing the crystals apart. That would be exactly the opposite to what the author apparently found, but he thought it was explained probably by the fact that all the metals contained gas; that when they were worked the gas cavities became condensed into a smaller compass, and consequently the density of the metal was increased. If the metal was heated it softened, and the gas expanded and forced open the metal to some small extent, at any rate enough to make the difference in the specific gravity which the author found. He merely threw that out as a suggestion, because he did not feel that the density of the metal ought to be decreased in the way the author stated it was.

Dr. WALTER ROSENHAIN (Member of Council) said he had not had an opportunity of studying the paper as closely as he would like to have done, as he had been away from the country, and he had not had time since his return on the previous evening to give it the attention it deserved. He was very much interested in it, because it dealt with a piece of work done on lines more elaborate than, but somewhat similar to, work which Sir Alfred Ewing and he carried out some twelve years ago. In the first place he desired to say a word of criticism on the experimental method adopted, namely, the use of the scleroscope for determining the hardness of metals of that kind. The scleroscope was a useful instrument for rough determinations of hardness when the hardness was considerable, but for soft metals, such as those dealt with in the paper, he had found it to be, after extensive attempts, distinctly unreliable. The actual amount of rebound was so small that the errors of reading and errors arising from want of adequately solid support for the specimens, particularly when the metal was used in the form of thin sheets, as was frequently the case, became exceedingly large. He did not think that the curves obtained with it were as satisfactory as one would have wished. They gave a general indication of what investigators had known for a long time happened in other metals, that they began to soften at a moderate temperature. With regard to the question of the "proper" annealing temperature, the author apparently took the view that "proper" annealing was annealing down to a condition of physical stability, *i.e.* getting down to the condition when no further change in the crystal size would take place. The logical outcome of that view would be to anneal until one got down to the condition of a single crystal. That would be "proper" annealing if one carried the suggestion out to its logical extreme. He did not think, however, the author would wish to do that, because he would have considerable difficulty in handling alloys in that condition. Therefore, as Professor Huntington had pointed out, the question of proper annealing was not necessarily determined by finding a temperature at which a considerable crystalline growth took place in a few minutes; it was a matter of mechanical testing. As regards softening accompanying recrystallization by annealing, that was a metallurgical commonplace for many years, and it was interesting to find it confirmed in the case of gold. There was one point, however, to which he desired to call attention, namely, that it was a little misleading to have the elongated crystals shown vertically in one figure and horizontally in the others. With regard to the softening of lead at the ordinary temperature he disagreed with the author in his view, that lead could not be hardened. Lead could be and was hardened very materially, as he had proved by observation by the Brinell method. He had repeatedly done that. If one took a casting of lead and determined its Brinell hardness, which could be determined quite satisfactorily by taking an impression on the casting, and then took a piece of the casting and crushed it into a flat sheet and took an impression of it, a considerable difference would be obtained if it was done soon enough. If it was done a week or two afterwards it was perfectly true that a considerable amount of softening had taken place; and as he (Dr.

Rosenhain) and Sir Alfred Ewing proved in the paper to which the author had referred, that softening became complete at a period somewhere of the order of six months, and was accompanied by a distinct crystal growth. In that case, where the process of recrystallization was very gradual, they obtained in the initial stages the curious ragged crystallization shown in a very characteristic way in Fig. 10 of Plate XX. The curious phenomenon was obtained of certain crystals growing at the expense of others, and that gave the ragged structure. But afterwards those things gradually filled out and rounded out, even at that temperature, if they were given enough time, until a structure was obtained, which was practically the structure given in Fig. 14, Plate XXI. It was only a question of time in the case of lead. In the case of zinc and cadmium, although the author suggested it ought to be observable in a period of six months, they had failed to find any signs of crystalline growth at the ordinary temperature. Possibly if the experiments were made at the present time, with the greater experience that was now available and more refined methods, they might be able to confirm the author's suggestion. At all events the paper was an interesting contribution to the study of the annealing of alloys. Professor Huntington had thrown out a suggestion as to the changes of density. He thought the change of density between the amorphous and the crystalline state was sufficient to account for the whole thing. If one had matter in a crystalline condition, and disturbed that regular molecular piling into something which was not regular piling, a decrease of density would be obtained, and when it was again arranged into regular piling then an increase of density occurred. There was first of all an increase of density due to working, then a decrease of density due to the formation of a small amount of amorphous matter, and then an increase of density again by annealing and restoring it to the completely crystalline condition.

Professor T. TURNER, M.Sc. (Honorary Treasurer), said the members had all read with very great interest the author's paper, which would be a permanent contribution to the study of the subject. The author had emphasized a fact which was well known, namely, that there was a definite minimum temperature for each metal or for each alloy to which it must be raised if annealing was to take place in a short time, and if, say five minutes or some other short period were used. But he had also shown that very slow annealing might take place at lower temperatures. Personally he was interested in the subject something like thirty years ago in connection with the letting down or tempering of steel by slow heating at low temperatures. The improvement in the cutting edge of a razor by merely putting it into boiling water appeared to touch on another branch of the same subject. He conducted a number of experiments by heating steel at various temperatures and for prolonged periods, and came to the conclusion that the steel was perceptibly softened at relatively low temperatures but by long heating. At that time there was no Brinell test and no scleroscope, so that his methods of testing hardness were much less perfect than they were at the present time. He agreed with Dr. Rosenhain's remarks to the extent that

the scleroscope was not a suitable instrument for testing the hardness, say, of lead or of tin or of zinc, because the rebound even with the magnified hammer was so low. But with alloys such as those the author had been treating, some of which had a rebound as high as 70—and he believed there were some that had a rebound even higher than that—he thought very fairly good results would be obtained. As to exactly what the scleroscope showed, there might be a difference of opinion. Personally, however, he had found the scleroscope an extremely useful instrument in connection with the worked hardness of metals as distinct from the ordinary physical hardness of unworked materials. The author and the speakers in the discussion had referred to the change in density which took place when metal was worked. It should be pointed out that that change of density was not always in the same direction. It depended partly upon whether the metal had been hammered or whether it had been drawn. Drawn metal might be lowered in density, while hammered metal might be increased in density. A very interesting point, so far as he was concerned, in reference to the observations of density was that the author recorded that the expansion taking place on softening was far greater in alloys than in pure metals. He believed that was a new observation; he did not remember having seen a record of that kind before, though it was known that metals expanded on annealing. He felt sure that the increased expansion of alloys had some connection with those changes in length which he had observed in connection with cast bars. They were what he had called volume changes. He had been told that they were not volume changes, but only changes in length, because the volume changes could not be measured. In cast alloys it was very difficult to measure the real volume change during the actual processes of solidification and subsequent cooling, owing to the difficulty of measuring in three directions at once; but apparently the author had measured a final change of density corresponding to the crystallization or the recrystallization of an alloy as being different from that of a pure metal. It was certain that if one took the trouble to cast a few bars, taking first two separate metals, and measuring the apparent change of volume, and then alloying those two metals together, a very definitely increased change of volume would generally be obtained. What the connection between these facts and Dr. Rose's experiments might be it was premature to say at the present moment, but he felt sure that it was a line of inquiry that would repay further study, and that the behaviour of the hardened alloys on annealing was closely connected with their behaviour when cast in a mould.

Mr. T. VAUGHAN HUGHES, Assoc.R.S.M. (Birmingham), said the subject of the paper was one which was rather dear to his heart, and he therefore could not refrain from making a few observations on it. To his mind the paper was full of practical import, and as had just been remarked, a number of to-day's papers were peculiarly so. He desired, in the first place, to ask one or two questions in regard to the preparation of test-pieces of the metals and alloys to which references were

made in the paper. Could the author indicate in his tables the medium in which the test-piece was annealed and when the surface was filed? The author referred to the process of hammering, which was a very indefinite operation. He would like to know what was done in each particular case. He also wished to know whether it would be possible to always define the mechanical treatment of the test-pieces by rolling them through a definite range and giving the percentage reduction before determining the hardness number. With regard to the scleroscopic method of testing hardness, which Dr. Rosenhain had criticised somewhat severely, there was no question about his assertion that it was not absolute. He doubted whether any of the tests for hardness or "tensility" were really absolute. For useful practical numbers, the method the author had adopted was largely employed. Of great interest were the forms of the curves shown by the author, especially the abrupt fall through a short temperature range, followed by a gradual slope. The latter indicated a state of things which was often presented in works practice. The statement is made that "it was all very well to anneal metals at a particular temperature, to obtain a softened product in a practical time, but a further soaking is required to effect the desired degree of softness." Explanation of this statement ought to be forthcoming by a further investigation of the cause of the gradual fall at the end of the sharp slope in the curves given in the paper. Another point of practical import was the very conclusive fact that annealing is brought about within comparatively small ranges of temperature (sometimes less than 50° C.) with consistent results in the degree of softness.

Dr. T. K. ROSE, in reply, said that Professor Huntington and Dr. Rosenhain had taken exception to the statement made on page 109 of the paper, that "It appears that such crystals must be formed by the time that the metal attains its minimum hardness and annealing can be said to be really complete." He was afraid he had used the word "annealing" there in rather a loose way. Perhaps he should have said "the establishment of equilibrium," because annealing was a word that he would not like to have to define. It meant so many different things to different people. He had no wish at all to make the statement that one must, in order to get the metal in the best possible condition for all uses, go on heating it after it had been softened until the last possible change in the direction of recrystallization and softening had taken place. From a practical point of view he was only dealing in the paper with the manufacture of coins from coinage alloys, and any practical conclusions he had drawn in the paper were confined to that subject. If any other practical conclusions could be drawn from the paper he would of course be exceedingly pleased. In minting it was necessary to have the metal soft, so that it could be permanently and readily deformed, and it did not matter much what its tensile strength might be. Professor Huntington asked whether the metal deteriorated when the new crystals were formed. That was a

subject on which he was at work at the present time, and he could not answer the question at the moment.

Professor HUNTINGTON said he put the question in that way because he had found considerable deterioration on annealing.

Dr. ROSE said that he was willing to agree that when metal was annealed at too high a temperature or too long it deteriorated in certain respects.

Professor HUNTINGTON said that occurred even when the crystals began to grow.

Dr. ROSE said that what he wanted to ascertain was whether the polygonal form of crystal had different properties from the ragged crystals. With regard to the density, he could not agree with Professor Huntington that the metals increased in density merely because the gas particles were expelled from the metal, or because the spaces containing gas particles were reduced in size and the gases compressed. He thought all metals when they were worked and rolled became harder and of higher density. A certain stage was arrived at, whether in wire-drawing or rolling, when instead of getting denser and harder the metal began to expand again and get softer, and those two stages were arrived at at the same moment. This appeared to prove, apart from theory, that the hard phase was a denser phase and not a less dense phase as Dr. Rosenhain suggested. [Dr. Rose wishes to add that his memory was at fault when speaking on this point. The only evidence in support of his statements rests on some unpublished experiments of his own on standard gold which became softer after long-continued rolling without any annealing, and also began to expand again. He can find no other evidence of this simultaneous action either in the case of metals or alloys, although it has been shown* that expansion occurs in wire-drawing. He recognizes, therefore, that pending further observations, the matter cannot be regarded as settled.] With regard to the use of the scleroscope for testing the hardness, Dr. Rosenhain thought it was good for hard metals but not so good for soft. He wondered whether Dr. Rosenhain had used all the necessary precautions when testing soft metals. He said that because personally he had spent a great deal of time and thought on the matter, and was of the opinion that for soft metals it was eminently suitable, while for hard metals it was not so satisfactory. He had arrived at that opinion owing to the fact that in hard metal it was impossible to get a uniform hardness throughout, so that the rebound continually gave a slightly different reading, as mentioned on page 88 of the paper. Soft metal could be obtained of the same hardness throughout, so that the same figure was always repeated, although sometimes it was a very small one. Anyone who used the scleroscope with due care would, he thought, agree that the results on soft metals were consistent, but he had not time to go

* Kahlbaum, *Journal of the Chemical Society*, vol. lxxxvi. 1904, Part II., p. 86; quoted by Dr. Beilby, *Journal of the Institute of Metals*, No. 2, 1911, vol. vi. p. 18.

into the question of what those results meant, except to point out that the scleroscope did not give the surface hardness of soft metals at all; it gave a sort of mean result for a layer of a full $\frac{1}{2}$ -millimetre thick. In the case of a hard metal it would give the mean hardness, or should he say "springiness," of a layer of less thickness. The Brinell method tested a layer of greater thickness. Dr. Rosenhain had referred to the difference in orientation of the crystals in Figs. 7 and 8, but that had of course nothing to do with annealing. Dr. Rosenhain had stated that the hardness of lead was greatly increased by working. It would be of interest to him if evidence was forthcoming bearing out that statement, because he had never seen any figures showing such an increase. Sir Alfred Ewing and Dr. Rosenhain did not state in their papers that lead softened at the ordinary temperature, and that the softening was complete in six months. They said that the crystals continued to grow at the ordinary temperature, and that the growth was probably not complete in six months. If the members looked at the beautiful photomicrographs in Sir Alfred Ewing's and Dr. Rosenhain's paper they would see that the crystals formed at the ordinary temperature were like the ragged crystals in Fig. 10, Plate XX., and not in the least like the crystals in Fig. 14, Plate XXI. Polygonal crystals occurred in the lead annealed at 200°, and his present belief was that the formation of such crystals was not a question of time but of temperature. The formation of small crystals in zinc at the ordinary temperature had been proved to occur by Timoféef only within the last few weeks.* That was the first of his predictions to be verified. With regard to Professor Turner's very kind remarks about the expansion of alloys, that was not a new observation, because it was shown to occur by Roberts-Austen in respect of standard gold as compared with pure gold in 1877. All that he had done was to show that the same thing took place in standard silver, as compared with pure silver. Mr. Vaughan Hughes had objected to the way in which he prepared his alloys. He could give full details of the method in each case, but the general method of preparation was stated on page 88, and would, he thought, be held to be satisfactory on careful consideration. Mr. Vaughan Hughes thought that having softened metals it was necessary to soak them at the annealing temperature for a long time to make them of good quality. This was not the case in mint work.

On the motion of the PRESIDENT, a hearty vote of thanks was accorded to Dr. Rose for his interesting paper.

COMMUNICATIONS.

Mr. O. F. HUDSON, M.Sc. (Birmingham), wrote with reference to Dr. Rose's observations on the recrystallization which took place on annealing cold rolled metals and alloys, that it might be of interest to refer to the

* *Journal of the Society of Chemical Industry*, September 16, 1912, p. 819.

results of experiments made by Dr. Bengough and himself on the annealing of brass alloys. These results were included in two papers given at previous meetings of the Institute,* and the conclusions drawn from them appeared to be similar to those arrived at by Dr. Rose. Thus in the case of 70/30 brass, dealt with at length in the second of the papers referred to, it was shown that complete recrystallization was produced by annealing the cold-rolled alloy for half an hour at a temperature of not more than $500^{\circ}\text{C}.$, and that a very rapid and decided growth occurred at higher annealing temperatures. It was also shown that annealing for half an hour at a temperature of about $300^{\circ}\text{C}.$ produced little change in properties as shown by tensile tests, although the actual hardness was not measured, and that little or no visible recrystallization had taken place. On heating the alloy for a similar period at a temperature of $500^{\circ}\text{C}.$ the tensile tests showed that practically the alloy was in the annealed condition, while complete recrystallization had occurred with the production of a very distinctly finer structure than that of the original cold-rolled material. The alteration in the mechanical properties was rather less marked at higher temperatures, although the increase in the size of the crystals was very great, and annealing at $800^{\circ}\text{C}.$ or above gave a very coarse structure. The rapidity of crystal growth was matter of considerable practical importance. In many annealing operations all that was required was that the metal or alloy should be heated *up to* the necessary temperature, and it was not desirable that the work should be maintained for any length of time at that temperature.

Mr. F. JOHNSON, M.Sc. (Birmingham), wrote that Dr. Rose's paper would be greatly appreciated by all scientific and practical metallurgists.

It placed on record the results of numerous experiments, and brought out a number of most useful and important facts.

There was one important point which impressed the writer, and that had reference to the annealing of copper (Table XI, p. 100). Dr. Rose showed that, at a temperature of about $300^{\circ}\text{C}.$, pure copper became completely annealed after seventy hours, a state of things which did not occur by quickly annealing until a temperature of $400^{\circ}\text{C}.$ was reached. If pure copper became completely annealed after 70 hours at $300^{\circ}\text{C}.$, it seemed certain that a similar result would be arrived at by a more prolonged annealing below $300^{\circ}\text{C}.$, and, in fact, M. A. Le Chatelier had shown that electrolytic copper became absolutely annealed at $200^{\circ}\text{C}.$ That meant that steam pipes of electrolytic copper would soften at a steam pressure of 180 lb. As was generally known, arsenical copper pipes did not soften at so low a temperature, and other impurities such as nickel and antimony had the effect of raising the temperature at which copper became annealed. So that, where such impurities could be present without injury to the mechanical properties of the copper, they ought to be welcomed and not regarded with suspicion.

Dr. W. ROSENHAIN, B.A. (Member of Council), wrote that, in order to justify the statement that he made at the discussion, he had prepared

* *Journal of the Institute of Metals*, vol. i. 1909, p. 89, and vol. iv. 1910, No. 2, p. 92.

some samples of lead and had made Brinell tests on them. A fairly large ball (16 millimetres in diameter) and a light pressure (100 kilogrammes) was used, in order to obtain indentations of the same order of dimensions as those given by the standard ball and load on steel. The resulting Brinell numbers, which were, of course, very low, have been calculated by the formula of Benedicks, the hardness number being obtained by multiplying the load in kilogrammes by the fifth root of the radius of the ball and dividing by the square of the area of the indentation. He (Dr. Rosenhain) used three specimens of lead: sample 1 was a flat casting about $\frac{3}{8}$ inch thick, very slowly cooled in a metal mould; sample 2 was a cylindrical casting about $1\frac{3}{4}$ inch high and 1 inch in diameter, very quickly cooled from fusion; while sample 3 was $1\frac{1}{4}$ inch high, slightly conical and slowly cooled. The Brinell tests were made in all cases with a load of 100 kilogrammes acting for one minute. The hardness numbers obtained for the cast lead were: For sample 1, 0.126; for sample 2, 0.173; and for sample 3, 0.129. Samples 2 and 3 were then crushed under a testing machine until sample 2 had a thickness of four-tenths of an inch and sample 3 three-tenths of an inch, the crushing being done quickly and further Brinell tests being made immediately after crushing. The hardness numbers obtained were: For sample 2, 0.261; and for sample 3, 0.236. Those results bore out very definitely the statement made that lead was hardened very perceptibly by cold work. He proposed to carry the matter a little further by making additional indentations under the same conditions on those crushed samples at intervals of a month, in order to ascertain what, he thought, had been found in the original experiments, viz. that the lead gradually softened again at the ordinary temperature.

Dr. Rose, in reply to the communications, wrote that Dr. Rosenhain's results confirmed the observation made by Sir Alfred Ewing and Dr. Rosenhain in 1901, referred to on p. 105. The scleroscope hardness number of 1.5 for lead both before and after rolling, given on p. 103, was the result of readings recorded to the nearest 0.5, and some hours had elapsed after the metal was rolled before its hardness was tested. The result was evidently inconclusive and the experiment was therefore repeated three times, the scleroscope being read to 0.1, and the means of twenty consecutive readings taken as the hardness numbers. The castings were $\frac{1}{2}$ inch (12.7 millimetres) thick, 1 inch wide, and 3 inches long. They were rolled down to 1.7 millimetre thick, or in the ratio of $7\frac{1}{2}$ to 1. The ingot A was cooled from fusion at a moderate rate, B was cooled very quickly, and C very slowly. A was rolled at 10° C. Its hardness number before rolling was 1.69; immediately after rolling it was 3.32 (five readings only); three hours later it was 1.9, and the same figure was found twenty-four and forty-eight hours later. B was rolled at 13° C. Its hardness number before rolling was 1.68; immediately after rolling it was 2.96 (five readings only); ten minutes later it was 2.39; thirty minutes after rolling it was 2.07; one and a half hours after rolling it was 1.93, and forty-eight hours later it was 1.95.

C was rolled at 13° C. Its hardness number before rolling was 1.74;

immediately after rolling it was 3.07 (five readings); ten minutes later it was 2.33; thirty minutes after rolling it was 1.96; one and a half hours after rolling it was 1.89, and forty-eight hours later it was 1.91. A portion of it three weeks later was 2.08, and another portion after twenty-four hours at 100° C. was found to be 1.65.

The hardness immediately after rolling fell off after the first few readings had been taken, and the means of the first five were therefore given. The means of the first twenty readings were slightly lower. The exact means were given, although the second place of decimals was of no value. The softening at the ordinary temperature appeared to be practically complete in about half an hour.

The rapidity of the fall in the hardness was more marked than he had expected, but the scleroscope, like the Brinell tests, clearly showed a momentary hardening on working. The discrepancy between Dr. Rosenhain's results and his own on quickly and slowly cooled lead was probably due to the fact that the scleroscope tested the hardness of a thin layer at the surface which would not be affected by the rate of cooling, and the Brinell test gave the hardness of the interior, which had solidified under pressure in the case of the quickly cooled ingot.

He then made some experiments on lead rolled at lower temperatures and found much higher hardness numbers. Ingot D, after casting, had a hardness number of 1.76. It was rolled at a temperature of -7° C. and its hardness found to be 5 (ten readings). Five minutes later its hardness was 3, and half an hour later 1.94. Ingot E, hardness 1.8, was rolled at -15° C., and its hardness raised to 6. Ingot F, hardness 1.8, was rolled at -25° C., and its hardness raised to 7 (first three readings), which fell to 5 in a minute or two, *i.e.* by the time fifteen readings had been taken. Ingot G, hardness 1.8, was rolled at -45° C., rising to -35° C., and its hardness raised to 8½ (mean of first five readings, 8.4). A piece of ingot, G, after rolling, was kept at -35° C. for half an hour, when its hardness was found to be still above 8. Another piece was kept at 0° C. for half an hour and its hardness had then fallen to 2.5. Ingot H, hardness 1.78, was rolled at -30° C., and its hardness found to be 7. The hardness of a piece of it kept at -25° C. for half an hour was 6, that of another piece kept at -20° C. for half an hour was 4.5, and that of a third piece kept at 0° C. for half an hour was again 2.5. On cooling a piece of rolled lead, hardness 2, to -35° C., and keeping it at that temperature for half an hour, its hardness was found to be 2.1.

In the experiments, the ingots were kept in a bath of ether of the required temperature, and the rolls were chilled by wrapping them in cotton steeped in cold ether. After each passage of the metal through the rolls the lead was again cooled, and the heating effect of the work done on it was made evident by the boiling of the ether in which it was placed. The hardness was tested at the ordinary temperature, with the piece of lead gradually warming up. The temperatures given were therefore minima.

It was clear from those experiments that lead could be hardened by work to a greater extent than could be detected by rolling at the ordinary temperature, and could not be annealed in half an hour at

-35° C. It began to soften, however, below -20° C., and softened rapidly at 0° C. It softened still more rapidly (softening being practically complete in thirty minutes) at the ordinary temperature, but instantaneous annealing did not take place until some higher point. The results verified the expectation expressed on p. 105.

The growth of crystals in lead observed by Sir Alfred Ewing and Dr. Rosenhain in 1901 thus evidently took place after softening was practically complete.

Mr. Hudson had drawn attention to the previous work of Dr. Bengough and himself on the annealing and recrystallization of brass alloys. The general agreement between their results and those of the author appeared to show that the conclusions in the present paper could be extended to more complex alloys with certain qualifications. If more than one constituent was present, for example, it was probable that each constituent had its own critical range of annealing as long as it retained its individual existence, and therefore that the critical range of annealing of the alloy would be a more extended one than that of either constituent.

Mr. Johnson's useful communication raised two points on which further information was desirable. M. A. Le Chatelier* annealed copper for one hour at 200° C. and found that the breaking load was reduced, but appeared to consider at that time that a higher temperature of annealing than 200° C. was required for the breaking load to reach its minimum. He had been unable to trace the experiments in which M. A. Le Chatelier had "shown that electrolytic copper became absolutely annealed at 200° C." There were probably differences between the statical resistance to permanent deformation by extension (testing machine) and the dynamical resistance to permanent deformation by compression (scleroscope) in which viscosity came into play. Precise data as to the effects of particular impurities in raising the annealing temperature of copper seemed to be lacking, but there could be no doubt that Mr. Johnson was right in his general contention.

To sum up, the author desired to express his appreciation of the kindly encouraging spirit of the discussion. No exception had been taken to the conclusions which he had drawn except as to density. Doubts had been expressed whether the scleroscope readings could be trusted when dealing with soft metals, but although he thought these doubts were groundless, nevertheless it was to be observed that the main conclusions would not be affected even if the readings were regarded as containing notable errors. He was therefore glad to find that he was not called on to defend those conclusions, and could assume that they were accepted.

* *Revue de Métallurgie*, April 1896, p. 567.

THE EFFECT OF TEMPERATURES HIGHER THAN ATMOSPHERIC ON TENSILE TESTS OF COPPER AND ITS ALLOYS, AND A COMPARISON WITH WROUGHT IRON AND STEEL.*

BY PROFESSOR A. K. HUNTINGTON, ASSOC. R.S.M., F.I.C. (VICE-PRESIDENT).

THE tests included in this paper were made at various times between 1900 and the present year. As the method of heating the bars to the required temperature is believed to be different to any method hitherto described, and as it has been proved to be easy to carry out and to give reliable results, a detailed description of it may prove of interest and practical value.

One point which has been found of considerable importance in this method of testing is, that the elastic limit or the yield point can be taken, which is not the case when a heated bath or an electrically heated jacket is used.

As a result of having to consider generally only cold tests of iron and steel, engineers are in the habit of reckoning the elastic limit as 50 per cent. of the breaking load. It will be seen from the curves given in this paper that this method of estimating the elastic limit is not correct for iron and steel at temperatures above the normal, nor, as a rule, for other metals at any temperature.

METHOD BY WHICH THE TENSILE TESTS AT TEMPERATURES HIGHER THAN THE NORMAL WERE MADE.

The tests were made with a horizontal machine of the Kirkaldy type. This machine is provided with a saddle, which can be moved along the bed of the machine by hand-wheel or hydraulic pump. Attached respectively to the saddle and to the levers actuating the beam are two massive heads, (*a*) Fig. 1, in each of which there is a vertical slot, the slot being enlarged towards its inner end so as to form two

* Read at Autumn General Meeting, London, September 25, 1912.

vertical shoulders facing inwards (*b*). The test-bar (*c*) is screwed at each end into a cylindrical holder (*d*), the other end of which is screwed on to the end of a large bolt (*e*), which passes loosely through a hole in a rectangular block (*f*). These blocks fit loosely in the enlarged ends of the slots in the heads. When testing at high temperatures sheet asbestos may be inserted between the blocks and the heads.

The test-bars are of two patterns: (*a*) for use with high-temperature thermometers, (*b*) for use with a thermoelectric couple.

The pattern (*a*) is 18 inches long and 1 inch diameter, except at the middle, which is turned down to 0.5 inch diameter over a length of 2 inches. The ends are screwed for about 2 inches to fit the cylindrical holders, and at 0.5 inch from each shoulder a hole is bored centrally, Fig. 2, $\frac{5}{16}$ inch in diameter and 0.75 inch deep, to hold a thermometer. In order that the thermometer may be sufficiently enveloped by the bar, the drill is driven in until the point bulges the metal at the opposite side of the bar. Connection between the thermometer bulbs and the test-bar is ensured by means of a small quantity of a low melting-point alloy.

The pattern (*b*) is 5 to 6 inches long and 1 inch diameter, the middle being turned down to 0.8 inch over a length of 2 inches. About 1 inch at each end is screwed to fit the cylindrical holders.

In order to attach the thermocouple to the bar, a piece of asbestos sheeting,

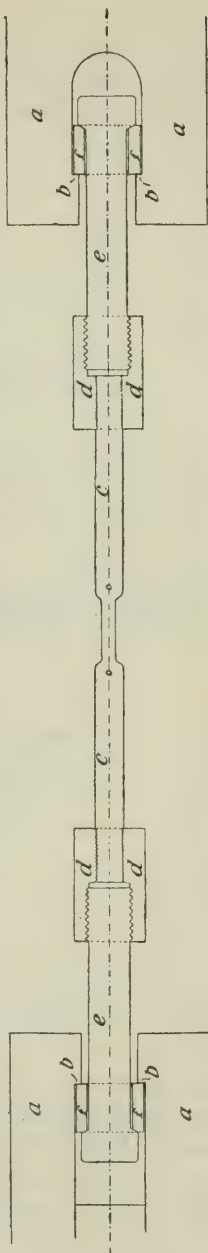


FIG. 1.—Plan (section) of heads and holders on testing machine, showing method of attachment to bar.

1 inch long and $\frac{1}{2}$ inch wide, is split down a little more than half way, and a small hole made through one side about the middle. The junction of the couple is inserted through the hole from the inside, Fig. 3 (*a*), so that the small knob is just

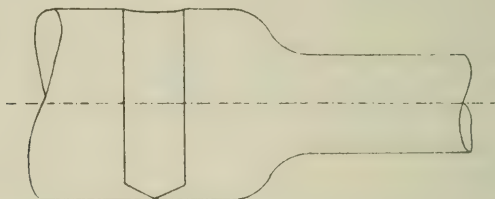


FIG. 2.—Section of test-bar about shoulder, showing thermometer hole. Actual size.

protruding on the outside. The asbestos and couple are placed on the bar with the junction of the couple touching the middle of the bar, and bound firmly into position by two or three pieces of thin wire, Fig. 3 (*b*). The curves, more particularly for electrolytic copper, copper-tin, and copper-

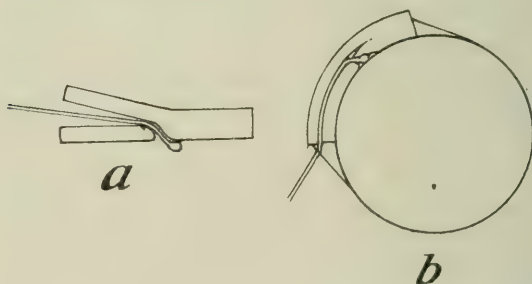


FIG. 3.—Showing method of attachment of wires of thermocouple to bar.

- (*a*) Couple inserted into prepared asbestos sheet.
- (*b*) Bound with thin iron wire in position.

aluminium, show that very good results can be obtained with high-temperature thermometers, but it is a saving of time to use an electrical pyrometer, which has also the important advantage of enabling bars of a larger diameter to be tested.

The bar is heated by placing a Bunsen burner under each end of the bar with pattern (*a*), and by means of a "bar

burner" with pattern (b), Fig. 4. The burner is 14 inches long, and made by Messrs. Fletcher, Russell & Co., the part under the test-bar itself being prevented from lighting by placing two overlapping pieces of sheet iron over the holes, so that only the cylindrical holders are actually heated by the flame.

Before placing the bar in the machine it has to be marked. A dark streak, about $\frac{3}{8}$ inch wide, of some suitable ink, is made on the central portion of the bar from shoulder to shoulder. When dry, a small mark is made near one shoulder with a fine centre punch, and with this mark as centre and a 2-inch radius, an arc is scratched across the other end of the ink streak, using spring dividers which have been sharpened. Another punch mark is made on the middle of the arc, and a similar arc made at the first end of the bar, using the second punch mark as centre.



FIG. 4.—Bar Burner.

When the bar has reached the required temperature, and this is quite steady, the length between the left-hand centre punch mark and the corresponding arc is measured by placing one point of the dividers in the hole, and laying the other point on the arc and viewing the arc through a hand lens. A suitable load is then placed on the bar, and the bar measured with the load on. If no stretch is observed, the load is slowly increased until a distinct stretch is observed, when the load is taken off and the bar measured. If no stretch is observed with the load off, the load is slightly increased, and the bar again measured with the load off, this procedure being repeated until the bar shows a permanent stretch. The load required to produce this is taken as the yield point. It is found that a stretch of .003 inch can be observed by this method. After the yield point is reached, the load is increased slightly and the bar measured with the load off. If the previous load was really the yield point, an

increased stretch will be observed out of all proportion to the extra load applied. If this observation is satisfactory, the bar is "broken out," the load being increased rapidly until the bar breaks, no intermediate measurements usually being taken.

With test-bars of pattern (a) the thermometers are removed before "breaking out" the bar.

TABULATED RESULTS OF TENSILE TESTS AT TEMPERATURES HIGHER THAN THE NORMAL.

The metals and alloys used in the following tests were specially free from impurities and were annealed. A "trace" in all the analyses means less than 0.005 per cent.

Test-bars of pattern (a) were used in all cases except that of copper-nickel, for which the test-bars were of pattern (b).

TABLE I.—*Electrolytic Copper, March 13, 1906. Rolled 1-inch Rod.*

Analysis.

Arsenic	trace
Antimony	nil
Bismuth	0.0005 per cent.
Selenium	trace
Tellurium	trace

TENSILE TESTS.

All test-bars annealed 2 hours at 600° C.

Temperature of Test.		Yield Point. Tons per Square Inch.	Breaking Load. Tons per Square Inch.	Elongation per Cent. on 2 Inches.	Reduction of Area per Cent.
Degrees F.	Degrees C.				
55	13	2.86	13.97	56.0	66.3
200	93	2.58	12.41	56.0	68.6
300	148	2.64	11.46	55.0	67.44
400	204	2.85	10.55	53.0	66.3
450	232	2.29	9.61	49.5	61.5
650	343	2.30	6.91	25.0	28.2
750	399	2.33	6.42	27.0	27.16
850	455	1.71	5.43	21.0	26.0
900	482	1.42	5.13	20.5	29.4
900	482	2.00	5.17	23.5	25.1
950	510	1.43	4.17	23.0	26.0
1000	538	0.5	3.7	32.0	45.2

TABLE II.—*Arsenical Copper, December 21, 1900. Rolled 1-inch Rod.*

<i>Analysis.</i>		Per Cent.
Arsenic		0·234
Antimony		nil
Bismuth		0·009
Selenium and tellurium		trace

TENSILE TESTS.

All test-bars annealed 2 hours at 600° C.

Temperature of Test.		Yield Point. Tons per Square Inch.	Breaking Load. Tons per Square Inch.	Elongation per Cent. on 2 Inches.	Reduction of Area per Cent.
Degrees F.	Degrees C.				
100	37·7	2·27	13·75	50·5	64·0
200	93·3	2·27	12·95	57·5	70·8
300	150·0	2·27	11·81	51·5	70·8
400	204·0	1·98	11·07	49·0	78·8
500	260·0	1·98	9·71	50·0	66·3
600	316·0	1·98	9·32	47·5	58·5
700	371·0	1·98	7·52	16·0	26·0
800	427·0	1·70	5·37	10·0	15·3

TABLE III.—*Copper-Tin, February 9, 1900. Rolled 1-inch Rod.*

<i>Analysis.</i>		Per Cent.
Copper		97·673
Tin		2·408
Lead		0·024
Nickel		trace
Iron		trace
Manganese		nil.

TENSILE TESTS.

Temperature of Test.		Yield Point. Tons per Square Inch.	Breaking Load. Tons per Square Inch.	Elongation per Cent. on 2 Inches.	Reduction of Area per Cent.
Degrees F.	Degrees C.				
60	15·5	4·83	19·13	56·0	75·0
400	204·0	2·84	16·77	53·0	68·6
500	260·0	2·84	16·25	45·0	56·4
600	316·0	2·84	14·54	23·5	26·0
700	371·0	2·55	11·36	21·0	22·5
800	427·0	3·12	12·97	36·5	29·4
870	465·0	2·84	12·31	38·5	42·2

TABLE IV.—*Copper-Nickel, July 23, 1909. Rolled 1-inch Rod.*

Nickel about 12 per Cent.

TENSILE TESTS.

All test-bars annealed $\frac{1}{8}$ hour at 650° C.

Temperature of Test.		Yield Point. Tons per Square Inch.	Breaking Load. Tons per Square Inch.	Elongation per Cent. on 2 Inches.	Reduction of Area per Cent.
Degrees F.	Degrees C.				
55	13.0	9.3	18.1	55.5	63.0
200	93.3	9.25	16.2	55.5	79.0
300	150.0	9.0	15.1	54.5	79.5
350	176.7	7.6	14.1	57.0	77.0
400	204.0	7.4	14.1	55.0	76.0
450	232.0	8.0	13.4	52.0	71.5
500	260.0	7.5	12.8	49.0	65.0
550	287.8	7.8	12.3	43.5	60.0
600	316.0	7.7	11.8	39.0	53.0
700	371.0	8.2	11.55	35.5	54.5
800	427.0	8.7	11.9	37.5	54.0
850	455.0	7.13	9.9	27.5	41.0

TABLE V.—*Copper-Aluminium, December 7, 1900. Rolled 1-inch Rod.**Analysis.*

	Per Cent.
Aluminium	7.15
Iron	0.115
Silicon	0.027

TENSILE TESTS.

In tests marked * test-bars were specially annealed in laboratory 2 hours at 600° C.

Temperature of Test.		Yield Point. Tons per Square Inch.	Breaking Load. Tons per Square Inch.	Elongation per Cent. on 2 Inches.	Reduction of Area per Cent.
Degrees F.	Degrees C.				
60	15.5	4.26	23.86	91.0	72.9
400	204.0	*4.93	20.94	81.0	58.2
500	260.0	*4.31	17.95	49.0	43.7
600	316.0	4.93	14.56	25.0	30.4
800	427.0	4.93	10.02	12.0	16.0
900	482.0	2.84	6.25	13.0	25.4

TABLE VI.—Copper-Zinc, January 16, 1900. *Extruded Rod.*

Zinc about 40 per Cent.

TENSILE TESTS.

In tests marked * test-bars were annealed 2 hours at 600° C. All other bars annealed, but temperature not recorded.

Temperature of Test.		Yield Point. Tons per Square Inch.	Breaking Load. Tons per Square Inch.	Elongation per Cent. on 2 Inches.	Reduction of Area per Cent.
Degrees F.	Degrees C.				
60	15·5	*5·96	26·13	50·5	66·3
400	204·0	*7·67	20·11	64·0	70·8
400	204·0	7·95	19·56	63·5	72·9
500	260·0	7·38	17·56	67·5	66·3
600	316·0	5·68	12·47	35·5	48·1
700	371·0	1·98	6·85	36·0	45·2
800	427·0	1·13	3·48	27·0	39·1

TABLE VII.—Mild Steel, March 23, 1900. *Rolled 1-inch Rod.**Analysis.*

	Per Cent.
Silicon	0·053
Sulphur	0·041
Manganese	0·401
Nickel	0·045
Phosphorus	0·138
Carbon	not determined

TENSILE TESTS.

In tests marked * test-bars were specially annealed in laboratory at 600° C.

Temperature of Test.		Yield Point. Tons per Square Inch.	Breaking Load. Tons per Square Inch.	Elongation per Cent. on 2 Inches.	Reduction of Area per Cent.
Degrees F.	Degrees C.				
*57	14	11·98	23·55	42·0	68·6
300	150	10·79	26·27	25·0	61·5
300	150	13·06	26·77	22·0	61·5
400	204	10·22	27·54	25·5	53·7
400	204	12·50	28·77	25·5	56·4
400	204	10·85	29·4	24·0	49·0
*400	204	12·5	28·27	24·0	59·0
500	260	10·22	30·0	23·5	53·7
500	260	10·0	25·6	34·0	60·5
600	316	9·09	27·9	29·0	56·4
700	371	7·38	24·31	35·0	64·0
800	427	9·09	20·34	30·0	68·6

TABLE VIII.—*Wrought Iron, March 28, 1900. Rolled 1-inch Rod.*

<i>Analysis.</i>						Per Cent.
Silicon	0.130
Sulphur	nil
Manganese	nil
Nickel	nil
Phosphorus	0.143
Carbon	not determined

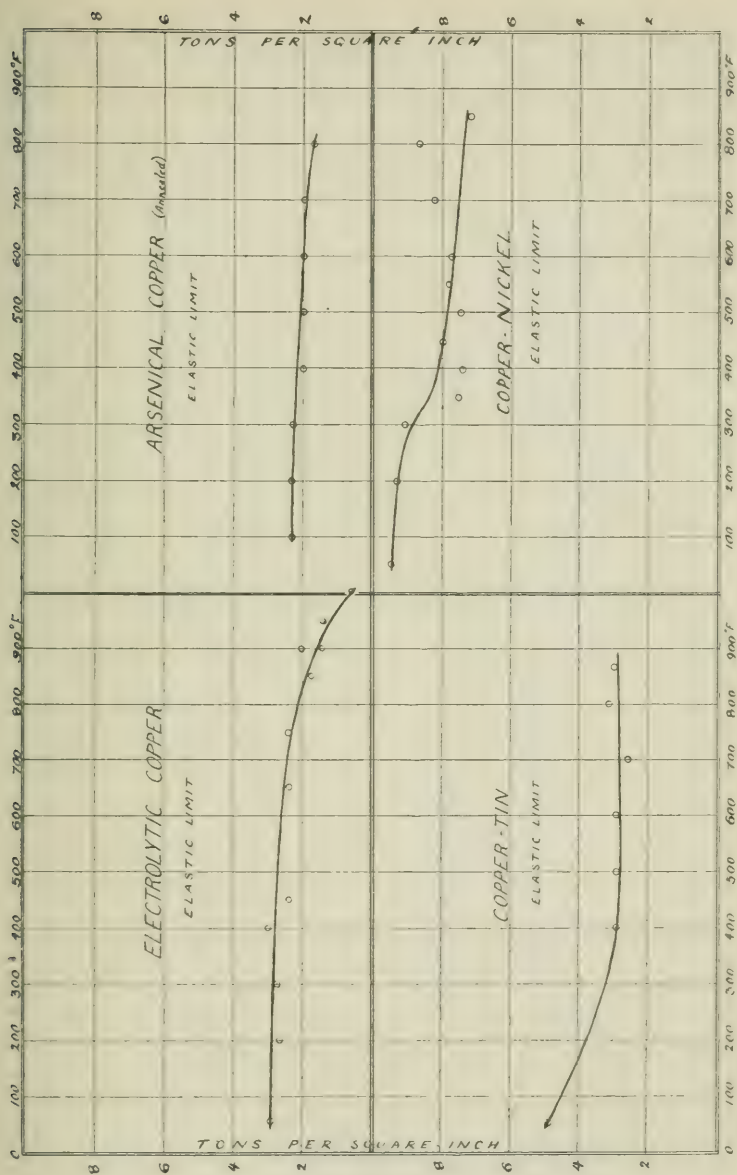
TENSILE TESTS.

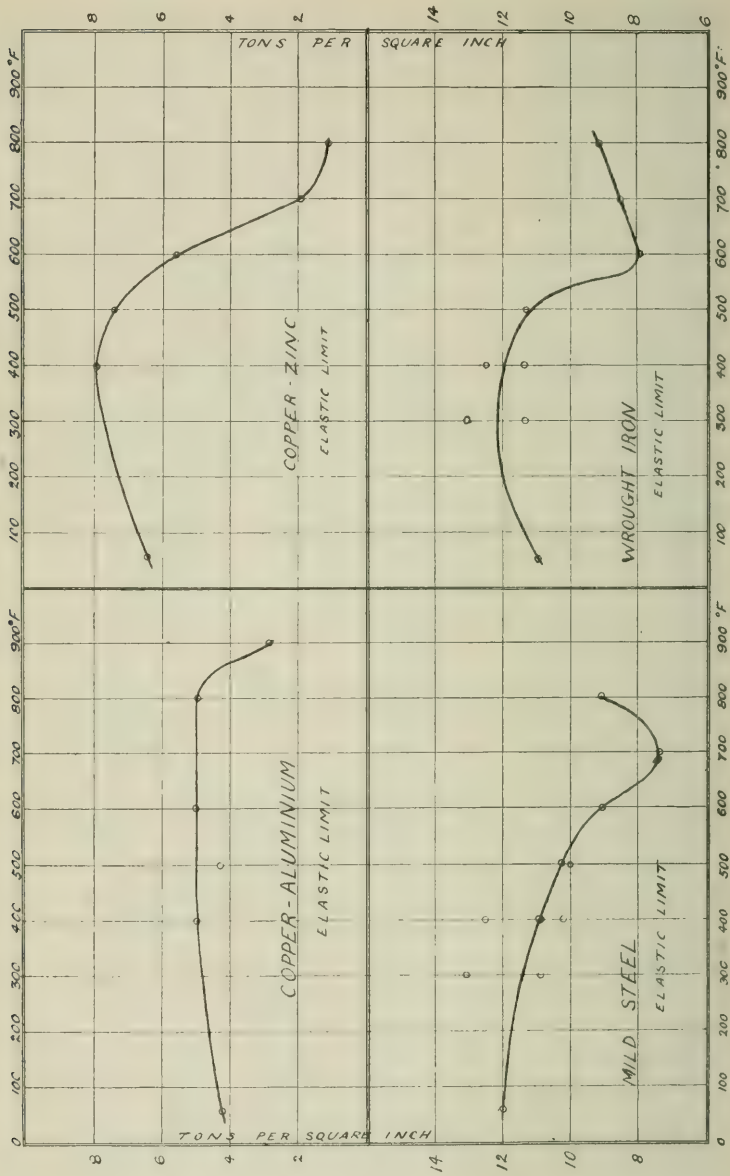
In test marked * test-bar was specially annealed in laboratory 2 hours at 600° C.

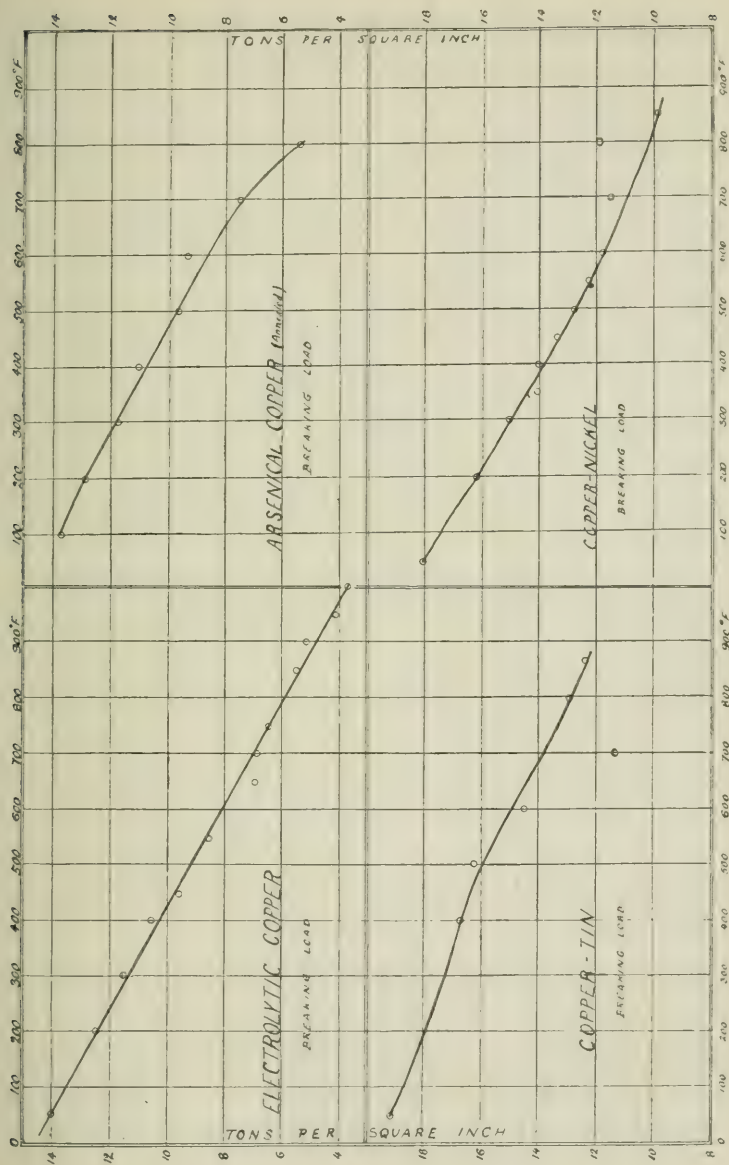
Temperature of Test.		Yield Point. Tons per Square Inch.	Breaking Load. Tons per Square Inch.	Elongation per Cent. on 2 Inches.	Reduction of Area per Cent.
Degrees F.	Degrees C.				
57	14	10.8	22.0	36.5	50.0
300	150	11.36	30.27	22.0	39.1
300	150	13.06	28.36	20.0	39.1
400	204	12.50	29.54	24.0	39.1
*400	204	11.36	28.77	20.0	39.1
500	260	11.36	30.00	24.5	36.0
600	316	7.95	28.45	23.0	36.0
700	371	8.52	25.00	26.0	36.0
800	427	9.09	20.59	20.0	45.2

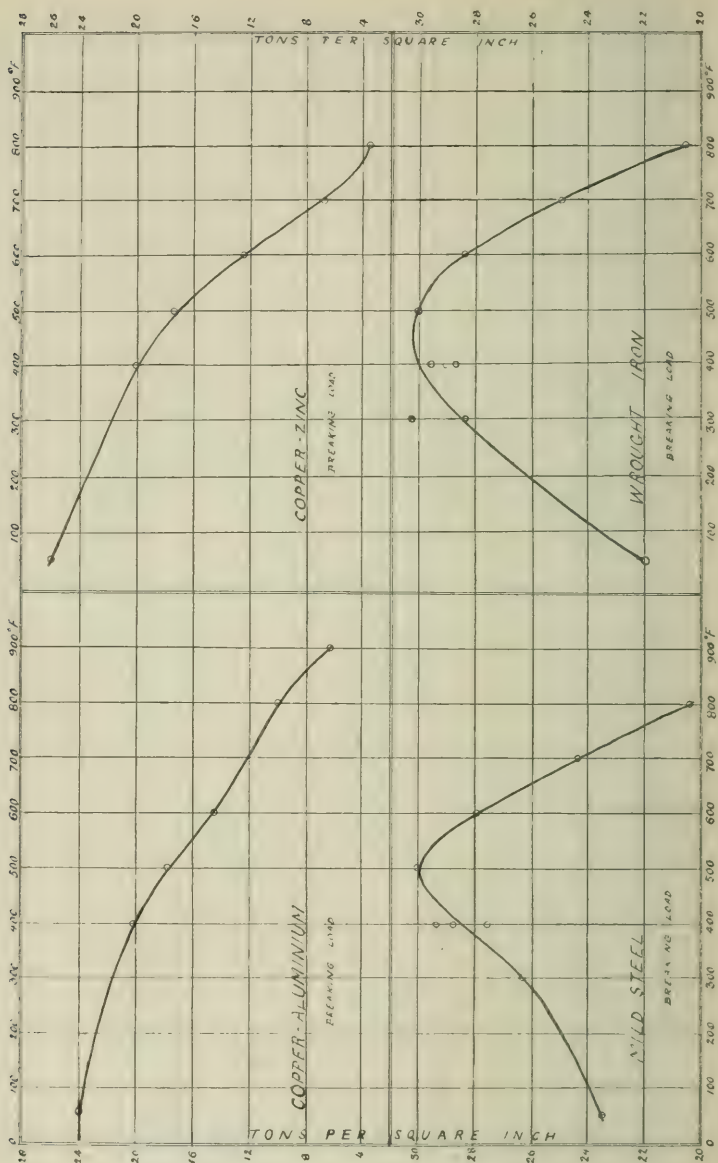
The foregoing results are shown graphically in the curves, pp. 135-142.

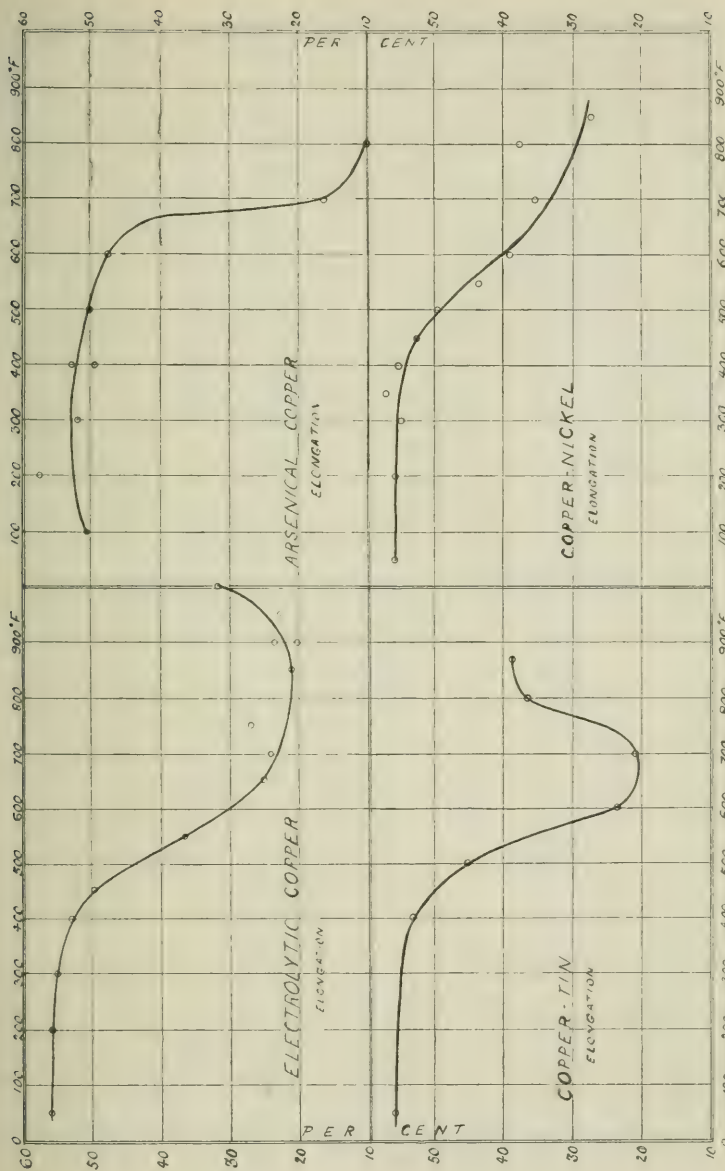
It will be convenient to take the electrolytic copper as a standard of comparison, and first of all to compare the copper alloys with it. Broadly speaking, they have the same characteristics. Contrary to what perhaps would have been expected, copper is the dominant partner. It has a distinct individuality, which is modified, but not extinguished, by the other metals. The curves for the elastic limits, or, more strictly speaking, the yield points, approximate to straight lines, except in the case of copper-zinc, which is probably explained by the large proportion of zinc. The irregularities in the copper-nickel curve are difficult to account for. The breaking-load curves still more closely approximate to straight lines, but show signs of being influenced by the second metal at the higher temperatures. The most distinctive curves are those for elongation and reduction of area. They show the preponderating influence

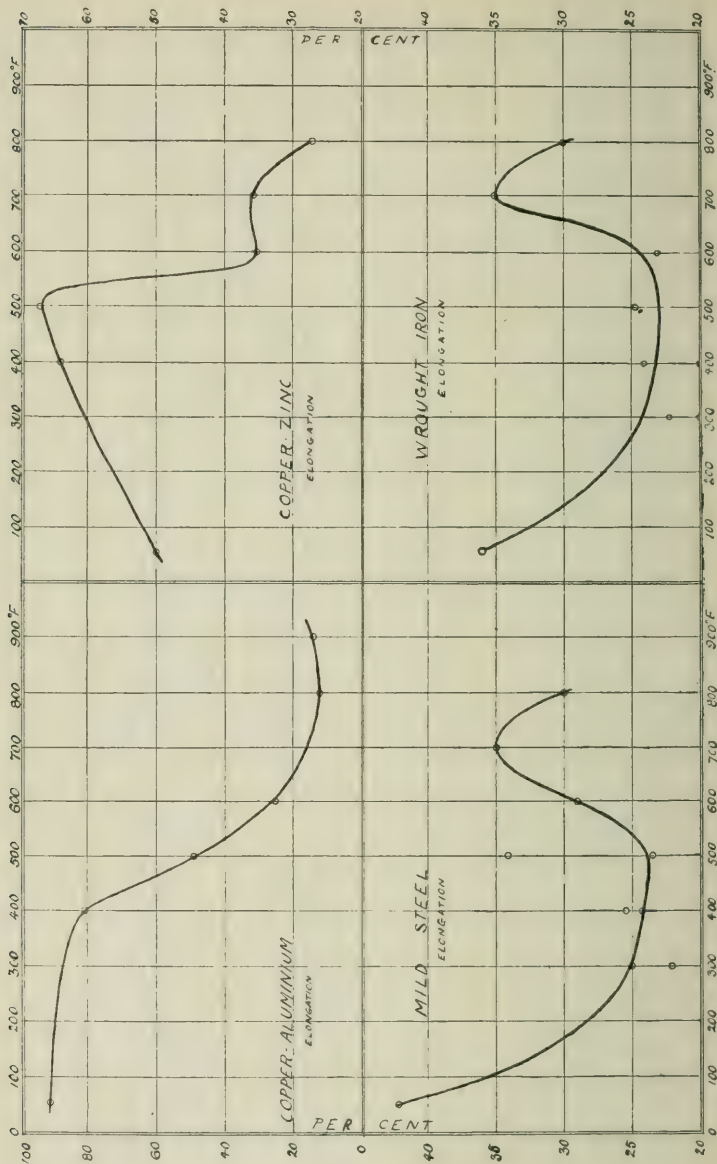


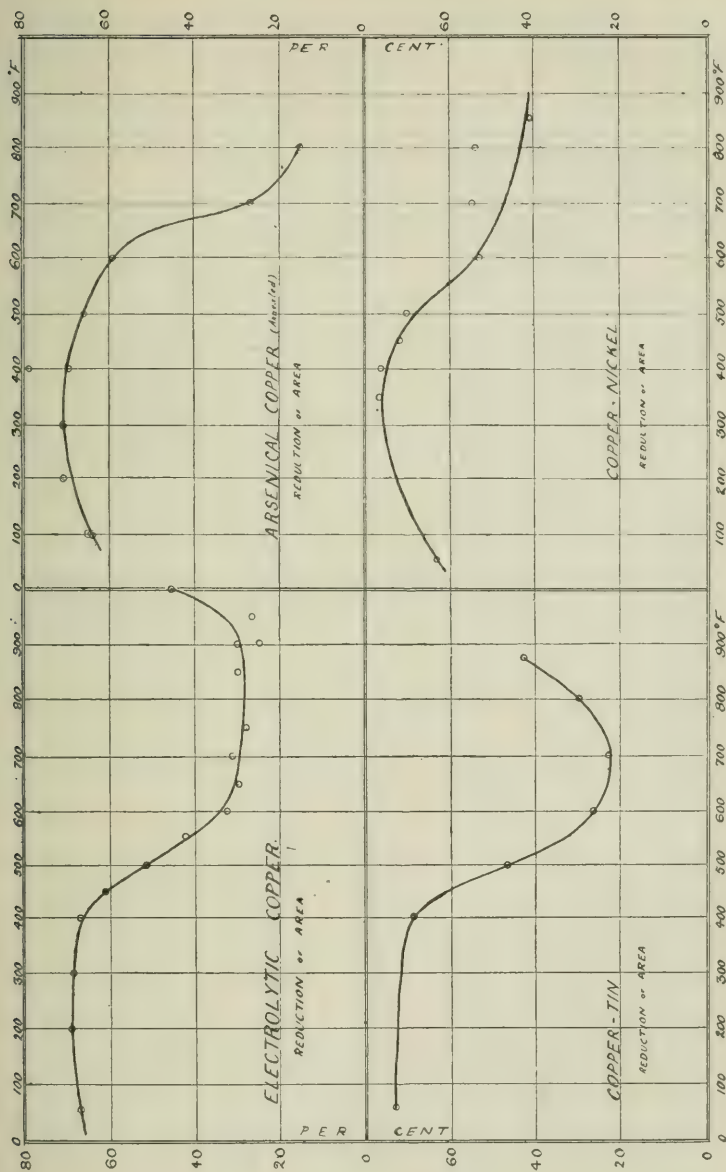


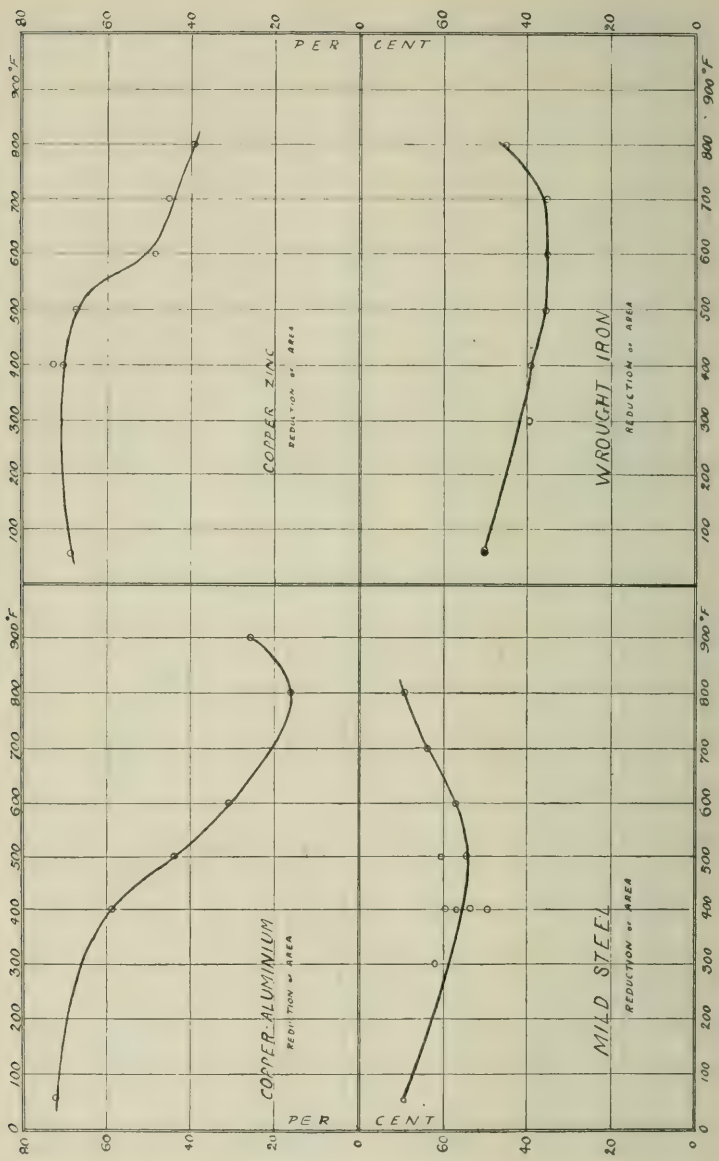












of the copper, and at the same time the modifying effect of the added metal. The more rapid rise above 800° F. in the copper-tin curve, the steady rise to 500° F. in the copper-zinc curve, and the close resemblance between the electrolytic copper and the copper with 7 per cent. of aluminium are all interesting. The reduction of area curves have a close resemblance to the elongation curves, except that the reduction of area up to 500° F. in the copper-zinc curve does not show the considerable rise which occurs in the elongation.

Although this Institute does not concern itself directly with iron and steel, their curves are inserted here for precisely the same reason that they were made, viz. for comparison, in order that it may be seen in what ways copper resembles or differs from these important structural metals. It will be seen at once that there are very great differences. In the yield-point curves the only resemblance to iron and steel is found in the case of copper-zinc. In the breaking-load curves iron and steel are markedly different from the others. In the elongation curves, instead of the approximately horizontal portion found in the case of copper and its alloys, except copper-zinc which shows a steep rise, iron and steel at once exhibit a rapid drop in elongation. In the reduction of area curves also there are considerable differences. Although there are not many points on the iron and steel curves, the close resemblance between these curves leaves no doubt as to their substantial accuracy.

It is fairly certain that engineers have hitherto expected a reduction of elongation with an increase in the breaking load in a given metal or alloy. They have been justified in this by the behaviour of iron and steel at atmospheric temperatures, and they are still justified at such temperatures as these metals would be used in the Arts. That they are not justified in applying this rule to copper and its alloys is manifest from an examination of the curves in this paper. It will be seen that, whilst the breaking loads are essentially straight-line curves, the elongation curves are contorted in perfectly definite ways, which, however, have no relation to the breaking loads. These are exceedingly interesting points and worthy of further study. It is somewhat remarkable that they have escaped observation

and investigation so long. That they have done so is probably due to the fact that in such experiments as have been made, insufficiently pure metal has been used in some cases, or the points observed may have been taken too far apart, or the test-pieces may not have been suitably annealed to make the tests comparable; not improbably the carrying out of the tests has left something to be desired in some detail or other. If the metal is not annealed after leaving the rolls annealing will take place during the tests, which will affect the shape of the curve.

It is difficult to conceive that the definite and strongly marked changes in direction in the elongation curves are not due to molecular disturbances. It is still more difficult to imagine these marked molecular disturbances leaving the breaking loads unaffected to a corresponding extent. Yet that is what takes place in the case of copper and its alloys, and with iron and steel above a certain temperature.

The range of temperatures given in this paper is restricted to such as might occur during the use of these metals and alloys in the Arts. What occurs during the manufacture and working of these metals and alloys is a different matter altogether and was not the object of the investigations. Numerous tests of other kinds than tensile were also made, which cannot be described on this occasion. It is intended to get out the curves for nickel, for which purpose rods were obtained some years ago.

The tests contained in this paper were carried out by different assistants, most recently by Mr. Licence and Mr. Baker. The Author takes this opportunity of expressing to all of them his gratitude for the zeal and efficiency which has invariably characterized their work.

DISCUSSION.

Dr. WALTER ROSENHAIN (Member of Council), in opening the discussion, said that the author in speaking on a previous paper had referred to a person called the devil's advocate. Professor Huntington would probably be amused to find him (Dr. Rosenhain) also playing that part for once, but he was inclined to play it on the present occasion. There appeared to him to be one or two things in connection with the paper which required further consideration. Once again he started with the experimental method. He could not feel that the method adopted by the author had any advantage, except that of allowing the determination of the yield point by means of dividers; but with regard to accuracy of temperature measurement he thought it left everything to be desired. If he understood the method rightly, it consisted in a horizontal test bar which was heated at the two end portions, and the portion under test was heated from the ends by conduction. The cooling of the bar from the surface by radiation and the heating from the ends implied a temperature gradient more or less considerable within the mass of the metal under test, and he thought that was a very serious defect of the method, so serious as in his eyes to condemn the results obtained. Then the author went on to criticize the work of others by saying that they had missed certain points, probably because they had used insufficiently pure metals, the points observed being too far apart, and a number of other general criticisms which he thought required a great deal of substantiation. He spoke as one of those others who had done a great many tests on metals at high temperatures, and personally he emphatically denied that any of Professor Huntington's suggestions applied to that work. Nevertheless that work and its results did not agree with Professor Huntington's. He thought it must be left to others or to the authors of other experiments to say who was right, and he was perfectly content to leave it in that way. The tests which were not in agreement with the author's, and of which he was thinking, were on the copper-aluminium-manganese alloys, and certainly all the conditions to which the author referred had been carried out in his (Dr. Rosenhain's) tests at least as completely, and perhaps more completely, than in the author's own work. He therefore thought the discrepancy required some other explanation. The only explanation he could suggest was that the temperature measurements in the method used by the author were not as reliable as they might be. That might displace the curve one way or the other, but he could not see that it would give a different shape of curve. The only explanation of that was that, in the author's experiments, one was dealing not with a bar of uniform temperature but with a bar hotter at the ends than in the middle and hotter in the centre than the outside, radially. How much hotter it was he did not know; that was a matter for measurement, but the author assumed that the rest of the bar was at the same temperature.

Professor HUNTINGTON, interposing, said that was not at all the case. Dr. Rosenhain would find the two methods described in the paper. In the original method the bar was heated towards the ends and thermometers used. In that case very careful measurements were made of the difference in temperature at various points along the tested portion, and it was found there was not a difference of more than about two degrees when the heat was up at 600° or 700° ; that was only a very small difference. This had been since corroborated by using a pyrometer strapped on to the centre of the bar. He thought that even Dr. Rosenhain would admit that in that case a definite register of the temperature was obtained. The registration by the pyrometer was absolutely the same that was previously obtained when using thermometers. The whole thing was tried very carefully. The results recorded in the paper represented only a few out of many hundreds that had been made. If the paper was carefully studied it would be seen that the curves of the copper alloys were in such close agreement with what was obtained for copper and that there was no possibility of there being any error in the shape of the curve. That would be seen, for instance, in the elongation curves, which were the most prominent. If the electrolytic copper was compared with the aluminium-copper and the copper-nickel or the copper-tin, it would be seen they all agreed. He thought Dr. Rosenhain had rather pressed the point a little too strongly, because it was not a matter of a few experiments, but of a great many experiments carried out over many years with the express object of obtaining extreme accuracy. When he said that the experiments left something to be desired, he did not mean what Dr. Rosenhain implied that he meant.

Dr. ROSENHAIN (Member of Council) said he appreciated the friendly tone of the discussion, and naturally anything he had said was merely directed at getting at the truth of the matter. The whole point was, that there must be some explanation for the discrepancy, and he thought it was necessary to get that explanation. For instance, in the curves for breaking load given on page 137, there were certain points which suggested that the errors of the experiment were very considerable. In the elastic limit curve for wrought iron shown on page 136, there were points which were considerably away from the curve. The curves for mild steel were still further away, and in some cases—for instance, in the elastic limit curve for copper-nickel—a totally different shape might equally well be obtained. So that the argument for agreement was not so sound as one would like it to be. The matter required the closest possible study, and the author must certainly be given every credit for having studied it carefully. But it was not sufficient to condemn the results of others simply because they did not agree with one's own. He was sure all the members considered the paper was a very interesting contribution to the subject, and because it differed from others it was all the more interesting and valuable.

Mr. VAUGHAN HUGHES, Assoc.R.S.M. (Birmingham), asked the author whether he had taken any precautions to exclude oxygen or the effect of air in the higher temperature experiments?

Professor HUNTINGTON said he had not. He did not think it had any effect whatever.

Mr. VAUGHAN HUGHES said the curves seemed to possess the idiosyncrasies of those prepared by Dr. Bengough and Mr. Hudson in their papers read before the Institute.

Professor HUNTINGTON said that he was using not small strips but inch bars.

Mr. VAUGHAN HUGHES said he did not care how large they were. He simply asked whether any precautions had been taken to exclude oxygen in the course of the experiments.

Dr. C. H. DESCH (Glasgow) said that as the objections that had been raised, and were likely to be raised, on the paper turned on the experimental method, and as he was probably the only person present besides Professor Huntington who saw many of the tests actually carried out, it might be useful if he said a few words on that subject. He saw a large number of the tests carried out by Mr. Davison, who was then the assistant, and who took very great care in the work he performed. He certainly came to the conclusion that the method used for the purpose was a trustworthy one. It was quite true that the bars were heated from the end, and that there must be a temperature gradient between the two heated portions. The turned-down portion was only 2 inches long, and tests were made at the time with thermocouples which showed that the temperature gradient was not a steep one. Now and then it happened that the bar was irregularly heated, and in that case it always showed itself by a defect in the bar at the time of breaking, and in that the test was then rejected. It seemed on the face of it a rough method as compared with bath or electric furnace methods, but it was known from the experience of other workers how difficult it was to get a uniform temperature with an electric furnace. For example, Rudeloff had published a long series of results obtained with an electric furnace, and personally he considered those experiments were absolutely worthless. It was impossible to draw curves from Rudeloff's results. He knew that in later work—in Dr. Rosenhain's, for example—greater precautions were taken, but the difficulties of the electric furnace were so great that there was something to be said for gas heating. With perhaps the exception of the elastic limit the results obtained were in the main trustworthy. Although they did not agree with the results obtained from the alloys used by Dr. Rosenhain, that did not necessarily prove that they were wrong, because they were different alloys; and although there was a general resemblance between copper alloys it might not extend to the other series examined. On the whole he thought the experimental methods to which the author had called attention had proved themselves to be generally useful for the particular purpose required.

Professor A. K. HUNTINGTON, in reply, said that he was afraid he had already replied to the discussion to a very large extent. The only point to which he wished to refer was the iron and steel which Dr. Rosenhain more particularly referred to, and the elastic limit. All through, iron and steel were very much less reliable than copper and its alloys, a fact which he thought would be of interest to the Institute, which was a non-ferrous Institute. He had always found that the tests of copper and its alloys, taking different specimens, were much more regular than in the case of iron and steel.

The PRESIDENT thought the paper was of extreme importance to engineers, for the determinations the author had made of the yield points, especially those of arsenical copper, which was now so very largely used in locomotive firebox plates. In a firebox the plate was exposed to very high temperatures, and it was necessary that an engineer should know what he might expect the yield point of the metal to be in those temperatures. He rather differed from Dr. Rosenhain in what he had said with regard to the temperature measurements. The measurements might not be absolutely accurate, but he thought the temperature gradient could not be so great as seriously to affect the results obtained. There was one point in the paper, however, which, as the author himself pointed out, required further investigation, namely, the steep fall in the elongation curve of arsenical copper, as there seemed to be no connection between that curve and the breaking load curve. He was sure it would be the wish of the members to give the author a very hearty vote of thanks for his extremely important paper.

The resolution of thanks was carried with acclamation.

INTERCRYSTALLINE COHESION IN METALS.*

WITH AN APPENDIX ON THE FORMATION OF
TWINNED CRYSTALS IN SILVER.

BY WALTER ROSENHAIN, B.A., D.SC. (MEMBER OF COUNCIL),

AND

DONALD EWEN, M.SC.

(BOTH OF THE NATIONAL PHYSICAL LABORATORY).

THE crystalline structure of metals has received considerable attention from a number of investigators (¹), and as a result of their labours it is now generally accepted that pure metals in the cast or annealed state are aggregates of crystals. These crystals possess the essential character of all crystals in having a regular arrangement or orientation of matter within their boundaries, but they do not as a rule possess any regular geometrical shape. The form and position of the boundaries of these crystals is determined by the surfaces upon which adjacent outward-growing crystals meet one another. On a section cut through such an aggregate, the crystals appear as more or less irregular polygonal areas, such as are to be seen in the microstructure of any homogeneous metal. On a section which has been polished and etched, the boundaries between the adjacent crystals appear, under normal lighting, as dark lines whose thickness depends essentially upon the depth to which etching has been carried. The appearance of this dark line is generally ascribed to a difference of level between the adjacent crystals produced, by the fact that the etching reagent attacks the various crystals at different rates according to the orientation of the particular surface exposed by each.

Although the general crystalline structure of a pure metal is thus well understood, and the typical features of its microstructure are adequately explained, it would appear that the nature of the intercrystalline boundaries is worthy of much

* Read at Autumn General Meeting, London, September 25, 1912.

further study. While one thought of metals and other solid bodies as simple homogeneous masses or aggregates of molecules arranged either all alike or, at least, in a statistically similar manner throughout the mass, the phenomena of the cohesion of such a solid could be explained broadly by reference to the intermolecular attractions following some law depending upon the inverse of the square or of a higher power of the distance; but once the fact that metals are aggregates of crystals is accepted, the explanation of cohesion phenomena must also be carried further. Within the mass of any one crystal, where the molecules or groups of molecules are arranged either in "closest piling" or in some regular manner which, because it is stable, must entail a minimum of potential energy and therefore of intramolecular distance, cohesion can still be referred directly to intermolecular attractions; but where two such crystals meet—not on any regular crystal face but on a surface of very irregular shape—it becomes difficult to see how the molecules belonging to the two different systems of orientation can be brought close enough to one another to attain to a degree of mutual attraction comparable with that existing within the mass of the crystal. From some such general considerations as this, the view would be deduced that the intercrystalline boundaries should be surfaces across which cohesion acted less strongly than it does across any plane within a crystal. In the early days of metallography, in fact, the opinion was frequently expressed that the intercrystalline boundaries or "joints" were surfaces of weakness. It was first shown by one of us, working in conjunction with Sir Alfred (then Professor) J. Ewing (²), that the tensile fracture of a piece of good Swedish iron does not follow the intercrystalline boundaries but runs across the crystals. Later one of us (³) has furnished numerous examples of the manner in which the fractures of metals normally avoid the intercrystalline boundaries, and at the present time it has come to be generally accepted that in metals and alloys in what may be termed conditions of normal health, the fracture runs across the crystals and never along the intercrystalline boundaries. Cases where the fracture does follow the boundaries are, of course, known, but they

always indicate that the material is in an abnormal or damaged condition. A classical example of this kind was shown by Arnold (⁴) in 1896, when he found that the presence of 0.1 per cent. of bismuth in gold was sufficient to surround the ductile crystals of gold with a brittle envelope which readily fractured under a blow. This is an extreme example of the effect of a deleterious impurity in weakening the intercrystalline boundaries. A similar weakening of these boundaries, although for less obvious reasons, has been found and studied in steel by J. E. Stead (⁵), by one of us (⁶), and more recently by Humfrey (⁷), and some of these cases will be referred to again in the later part of this paper. At the present stage, the point which it is desired to emphasize is that the intercrystalline boundaries of normal pure metals are surfaces not of weakness, but of special strength. This fact is further supported by the view which is almost universal among those conversant with the microstructure of metals, that a fine-grained structure in which the intercrystalline boundaries are very numerous, is superior from the point of view of strength and reliability to a coarse-grained structure in which there are comparatively few such boundaries.

The behaviour of a pure metal under strain further illustrates the comparative strength and rigidity of the intercrystalline boundaries. The slip-bands diverge from the boundary in such a way as to suggest that the movement of the boundary has determined the manner in which slip should occur. The whole deformation, in fact, appears to occur as if the boundaries formed a species of network of harder and stiffer material than the crystals themselves, and that the slip of the crystals took place in such a way as to accommodate them to the shapes and positions imposed upon them by the boundaries.

We have thus the fundamental fact that the intercrystalline boundaries possess mechanical properties decidedly different from those of the mass of a crystal, and the fundamental difficulty of accounting for this specially strong cohesion across such boundaries by the simple mutual attraction of the two differently oriented groups of molecules which there abut upon one another. Some further explanation of this specially

strong cohesion is thus required. An explanation of that kind has already been advanced by one of us ⁽³⁾, and in many metals there seems no reason to doubt that such an explanation holds good. The view referred to is that the growth of crystals towards one another takes place not by the accretion of successive layers, but by the shooting out of dendritic arms or branches, which continue to grow until they meet one another. In favourable circumstances the branching dendrites of adjacent crystals will tend to interpenetrate one another to a certain extent, and thus to bring about a definite structural interlocking of the two adjacent crystals. While such structural interlocking may well be an important factor in intercrystalline strength, particularly in metals which readily develop dendrites, careful study of a large number of crystal-boundaries does not seem to show sufficient evidence that the process is universal enough to account for the whole of the phenomena. It would seem, in fact, that the interpenetration of dendrites chiefly serves to increase the area of contact between adjacent crystals rather than to produce actual dovetailing. The hypothesis is therefore a natural one that there may be some cementing medium which exists between adjacent crystals in the intercrystalline boundaries, and serves to secure the specially close adhesion of one crystal to another. The relative position of the two views, which are really supplementary to one another, may be explained by a rough analogy. The dendritic interlocking may be compared with the mortise and tenon with which a carpenter joints together two pieces of wood; while the supposed intercrystalline cement corresponds to the glue with which such a joint may be rendered still more secure; indeed, when glue is used the analogy between the jointed wood and the crystal boundaries goes still further, since efforts at separation frequently result in a fracture which runs through the solid wood rather than through the glued joint.

Taking the existence of an intercrystalline cement as a working hypothesis, the nature or composition of the cement must be considered. Since the intercrystalline cohesion is at least as strong in the purest possible metal as in less pure varieties, the suggestion that the cement consists of impurities,

more fusible metals, or eutectics, cannot be entertained. With our present knowledge of the solid solubility of metals in one another, many metals are known of sufficient purity to preclude entirely the view that the impurities can exist in any state other than that of solid solution throughout the mass of the crystals. The inevitable conclusion is that, if such a cement exists at all, it must consist chemically of the same material as the metal itself, differing from it only in the manner in which its molecules are arranged. This brings us to the conception that the intercrystalline cement consists of the same material as the crystals themselves, only differing from them in regard to the manner in which the molecules are arranged. Now Beilby (⁸) has shown that metals can exist under certain conditions in an amorphous condition, and we thus arrive at the view that the crystals are held together by a very thin layer of metal in the amorphous condition lying between the crystals and acting as a cement. The object of the present paper is to describe certain experimental considerations which appear to lend weight to this hypothesis.

The conception of the existence of an amorphous intercrystalline cement in metals has been put forward here as an original one, because that conception has been used as a working hypothesis in the authors' laboratory for several years past, and some earlier references to this view have already been published (⁹). During that time, however, several other authors have arrived at a very similar view. Thus Bengough, in his paper on "A Study of the Properties of Alloys at High Temperatures" (¹⁰), distinctly states this hypothesis, but without formulating any definite experimental evidence in support of it. Osmond, also, in the discussion on a paper by Grenet (¹¹), states the same hypothesis as follows: "When two grains possessing different crystalline orientations touched one another, their respective reticular systems could not interlock, and there was strong reason for the belief that there existed between the two grains a sort of amorphous envelope, the average thickness of which was of the same order of thickness as the crystalline molecule." Unfortunately the late M. Osmond had never, so far as the authors are aware, stated what these "strong reasons" were. Rather

curiously, a somewhat similar idea of the constitution of a solid crystalline aggregate has been arrived at on purely mathematical lines connected with the theory of elastic hysteresis, by Sears (¹²), who finds an explanation for some of the anomalies in the elastic behaviour of metals by supposing them to consist of crystalline grains held together by an amorphous cement. It will thus be seen that the conception of an amorphous intercrystalline cement has been arrived at quite independently by a number of investigators—a fact which in itself lends considerable weight to the hypothesis.

It will be desirable at this stage to define very precisely what the authors understand by the term “amorphous cement,” and to give some indication of the manner in which they imagine that such a substance may come to be formed.

The term “amorphous” is to be regarded as the antithesis of “crystalline.” The latter term implies fundamentally the idea of orientation, of regular, orderly arrangement according to some definite reticulation, such, for instance, as “closest piling,” with or without the polarities suggested by Ewing (¹³). “Amorphous,” therefore, implies the absence of such regular arrangement. Typical of matter in the amorphous condition is the constitution of any ordinary liquid. When such a liquid is cooled below the temperature at which it may crystallize, so as to become extremely viscous and “hard” without undergoing any critical change or crystallization, we have an “under-cooled liquid,” or—what comes to the same thing—an “amorphous solid.” Typical of these is ordinary glass.¹ Beilby (⁸) has shown that on the polished surfaces of metals, thin layers of metal exist in this amorphous condition, and he has also shown that, under severe stress, thin layers of metal may assume a temporary mobile condition, and may flow like a true liquid, and he has further pointed out that thin films of such amorphous metal are formed on the surfaces of slip within the crystals of a metal under plastic strain. It is now proposed to indicate the manner in which a thin layer of amorphous metal may be formed and may persist in the inter-

¹ The term “amorphous,” as thus defined, is identical with the sense in which that term has been used by Beilby, who first applied the term in that sense to metals. The idea that glass is an amorphous substance of the nature of an under-cooled liquid is of earlier origin, having been adopted by Tammann and others before 1904.

crystalline boundaries, even in the absence of strain. Bengough has suggested that the formation of such a layer might be the result of the opposing attractions of the two adjacent crystalline systems, but the difficulty of that view lies in the fact that it implies an essentially unstable configuration which would certainly break down on heating, whereas the experimental evidence in the possession of the present authors clearly indicates that the amorphous cementing layer remains in existence at the highest temperatures, up to within 100° C. of the melting points of several metals.

Expressed in the most general way, the view taken by the present authors is that in the minute interspaces which remain when adjacent crystalline systems of differing orientation meet one another, the forces at work are such as to prevent the crystallization of the last vestiges of the mother-liquor, which therefore retains the amorphous constitution of the liquid while it is cooled down to the ordinary temperature. The forces at work may possibly be of the nature of capillarity, but for the sake of clearness the authors propose to offer a hypothetical explanation on somewhat different lines.

The proposed explanation depends upon the concept contained in Osmond's remark quoted above, viz. that of a "crystalline molecule" or unit which is large compared with what one might term the liquid molecule. This concept implies that the act of crystallization from the liquid state requires not merely the orderly arrangement of the molecule, but also a grouping together of the previously-existing liquid molecules into larger molecules or groups of molecules which we may term the "crystal units." In the case of the water-ice transformation, it has been shown quite clearly that some such molecular aggregation takes place, since it is even possible to speak of a water-ice solution.

If the existence of a crystal unit consisting of a number of "liquid" molecules be admitted, the formation of a residuum of "liquid" molecules in the crystalline boundaries is readily explained. For, whatever the true nature of the crystal units may be, the genesis of a crystal may be regarded as the building up of a regular structure by the piling up of units of a definite shape in a regular manner. This

process is represented in a diagrammatic manner in Fig. 1, where A and B represent sections of two adjacent crystals showing the units or "bricks" of which each is built up. If we consider the region where these two systems abut against one another, we find that there are formed a series of interstices which are smaller than the crystal units or bricks. The liquid residue left in these interstices will then be unable to crystallize, for the simple reason that there will be no

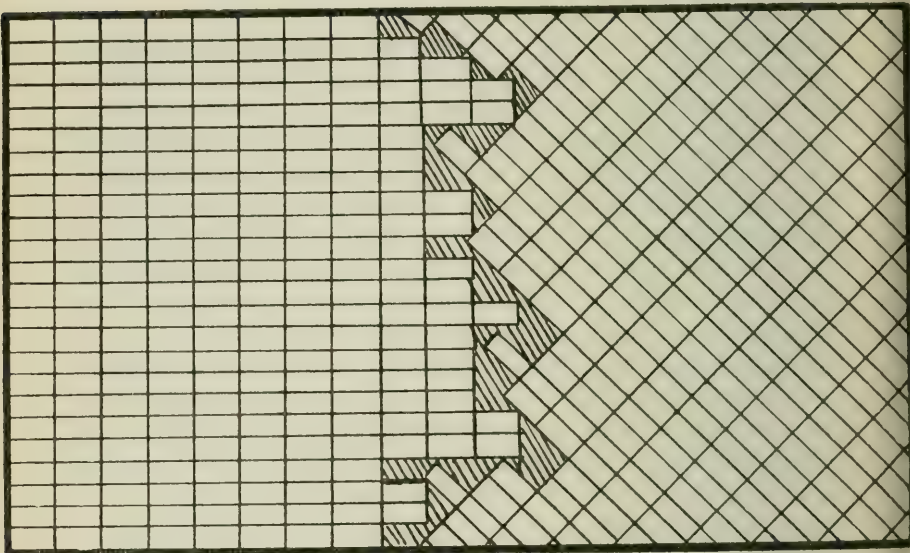


FIG. 1.

space for the aggregation of the "liquid molecules" to form a single "crystal molecule," and thus the portions shaded black in the diagram will remain in the amorphous condition.

From these conceptions, taken together with what is known of the properties of metals in the amorphous condition, certain consequences may be deduced. The first of these is that upon the strength and integrity of this amorphous cement the strength of the metal will largely depend. If the metal is exposed to any treatment which tends to remove or to injure this cement, the metal will become brittle or weak, and

such brittleness or weakness will only be curable by some mode of treatment which will restore the cement to its original condition. Metal in which this cement has been weakened or destroyed will display intercrystalline brittleness as distinct from cleavage brittleness, and this will be accompanied by a markedly low yield-stress under gradual loading in tension—the crystals, having lost the stiffening support of the intercrystalline cement, will begin to undergo bodily displacement as well as internal slip at a much lower stress than in the normal condition. It is a significant fact that over-heated steel which may still show a satisfactory ultimate stress frequently exhibits an abnormally low yield point. Beyond this fact, the recent observations of Humfrey (⁷) show an example of the manner in which suitable heat treatment may injure the intercrystalline cohesion of a metal. Humfrey in his experiments found that steel heated *in vacuo* and exposed to the action of very small amounts of oxygen—amounts too small to cause any marked tarnishing of a polished surface—showed extreme intercrystalline brittleness. Now in this experiment there is evidently a selective absorption of the oxygen by portions of the metal, since the exposed surface remains unoxidized. As we know that amorphous metal is more readily acted upon chemically than the same metal in the crystalline form, it appears probable that the oxidation has taken place in the intercrystalline cement, destroying its cohesion, and thus producing the intercrystalline weakness which results from such treatment.

Another consideration in connection with the properties to be expected in a crystalline aggregate held together by extremely thin layers of amorphous cement is connected with the dependence upon temperature of the properties of the crystals themselves and of the cement. Beilby has shown that the amorphous condition of a metal implies very great hardness and strength coupled with brittleness, in the sense that the amorphous material cannot undergo plastic deformation in the ordinary manner; on the other hand, the fact that a layer of amorphous material can spread over a polished surface under the action of surface tension, and also the semi-plastic condition which follows upon plastic strain in such a

metal as iron, indicate that under severe stress or pressure the amorphous metal may pass through a stage of temporary mobility. It is probably by the establishment of such a temporary mobile condition in the amorphous cementing material that intercrystalline boundaries can undergo plastic deformation in the cold. When a previously polished specimen of metal is plastically strained, in addition to the development of slip-bands, there is also a decided development of the intercrystalline boundaries — *i.e.* differences of level are developed between adjacent crystals. In metals plastically strained in the cold, the development of the boundaries in this manner is comparatively slight and the development of slip-bands very large. It has, however, been observed by Rosenhain and Humfrey in connection with experiments carried out as part of another research (¹⁴), that when such metals as copper or platinum are strained in a high vacuum at a high temperature (probably well above 1000° C. in the case of platinum) the development of slip-bands is slight and the differences of level formed at intercrystalline boundaries are large. A fuller investigation of these phenomena will shortly be described elsewhere, but enough has already been established by the observers named to justify the statement that there is a very marked difference between metal strained in the cold and the same material strained at a high temperature, and that this difference indicates that the boundaries become relatively much weaker as compared with the crystals themselves as the temperature rises. On the hypothesis of an amorphous intercrystalline cement this result is readily explained by the fact that an under-cooled liquid, while very hard and brittle at the ordinary temperature, becomes soft and viscous at high temperatures, while the reduction of internal friction which opposes slip within the crystals does not diminish with such extreme rapidity with rise of temperature. Up to a certain temperature, we should thus expect the law of the temperature-strength curve to be that of the diminution of internal solid friction, but at that point the softening of the cementing “liquid” would overtake the softening of the crystals, and from that temperature upwards the temperature-strength curve would follow the decrease of

the viscosity of the liquid with increasing temperature. Inflections in the temperature-strength curve corresponding to this view have already been found by Bengough, although he has explained them in a different manner⁽¹⁰⁾.

Having considered these classes of facts which are at all events perfectly consistent with the hypothesis advanced by the present authors, certain further aspects of the question may be discussed which lead to considerations capable of direct experimental verification. These relate to the behaviour of pure metals when heated in a high vacuum. It may be mentioned that the authors' interest in the present subject was first evoked by the observation of the striking fact that a specimen of such an extremely ductile metal as pure silver can be made brittle by continued heating *in vacuo*.

It has been shown by Beilby and others that the amorphous form of a metal is more soluble in acids or other reagents, and generally more readily acted upon by chemical agencies, than the crystalline form. The electric potential which exists between the same metal in the normal and the plastically strained condition when they are brought into contact with one another in an electrolyte is in itself strong evidence in support of this contention. It is a rational step to consider that if the amorphous form is more soluble, it will also possess a higher vapour-pressure than the crystalline material at the same temperature. If one accepts the view that the amorphous form is in reality identical with the highly under-cooled liquid, the conclusion that the vapour-pressure of the liquid phase will be higher than that of the crystalline phase is justified by analogy with the known cases where the two phases can be examined at the same temperature. If, then, the amorphous form has a higher vapour-pressure at a given temperature than the crystalline, a mass of metal consisting to a larger extent of the amorphous form should under similar conditions of temperature and pressure show a greater loss of weight by volatilization than a mass of the same metal more completely in the crystalline state. This is a conclusion which should be capable of experimental verification, and the authors have attempted to carry out experiments on these lines.

At first sight it would appear that a specimen of metal

consisting largely of the amorphous form could be obtained by utilizing a severely strained specimen, and that a comparison might even be obtained by simply heating together two specimens, one of which had been polished and left in that condition—*i.e.* with a thin surface layer of the amorphous form, while the comparison specimen had been somewhat deeply etched in order to remove the surface layer of amorphous metal as completely as possible. A little further consideration shows, however, that during the heating-up of such specimens the unstable surface layer of amorphous matter on the one specimen would be given every opportunity to resume the crystalline form—and microscopic observation of specimens thus heated clearly shows that this really occurs. For that reason the difference in volatilization between the etched and the unetched specimen would be very slight. An actual experiment made with two specimens of very pure silver showed that only a very minute difference in loss of weight could be observed. In the actual experiment two specimens of silver, weighing 3.2347 and 3.3510 grammes respectively, were heated in a vacuum of less than 0.003 millimetre, as measured by a McLeod gauge, for three hours to a temperature of 865° C., and it was found that the previously polished and etched specimen had lost 0.0901 gramme, while the specimen which had been polished but not etched had lost 0.0876 gramme. As far as it goes, this result confirms the view that the amorphous material produced by polishing or by strain resumes the crystalline condition during annealing, but in any case this experiment is lessened in value by the fact that it represents the first hours of heating *in vacuo*, during which specimens of metal always lose a relatively large proportion of gases—a circumstance which has led the authors in their more important experiments to reject the indications obtained during the first few hours of every heating of a fresh specimen.

Finding, thus, that amorphous metal resulting from any kind of strain is too unstable to be examined in regard to volatility at high temperatures, the authors devised the following method of procedure. If two specimens of the same metal can be prepared so that one of them consists

of a few large crystals, while the other consists of a very large number of small crystals, the area of intercrystalline boundary present in the two samples will be very different—there will be a very much larger quantity of boundary in the finely crystalline specimen than in the coarsely crystalline one. If the intercrystalline boundaries are the seat of an amorphous cementing layer, and this amorphous substance is more volatile than the crystalline metal, then if two such specimens are heated for the same time to the same temperature in an identical vacuum, the finely crystalline specimen should show a decidedly greater loss of weight than the coarsely crystalline one. During the first few hours this effect might be masked by the fact that the metal was losing occluded gases at a rate comparable with the rate of volatilization, and the amount of gas contained in the two specimens might be different according to the method pursued in their preparation. When the bulk of the gases has been removed, however, the other effect should become apparent in a regular manner, although, owing to the exceedingly minute quantities of amorphous material supposed to exist in the intercrystalline boundaries, the effect to be looked for might be a small one. It is, however, to be expected that if volatilization really occurs from the intercrystalline boundaries in the manner suggested by the authors' hypothesis, certain secondary effects will be produced. One of these will be that the intercrystalline cohesion of the metal will be weakened, and the specimens will ultimately exhibit intercrystalline brittleness. That this effect occurs in the case of silver has already been mentioned. A further effect is that the minute fissures resulting from the volatilization of the amorphous cement will allow of evaporation from the crystal surfaces abutting upon the boundaries, so that the excess of loss of weight to be looked for in the finely crystalline material will be larger than the mere weight of amorphous matter present to begin with, and microscopically one might hope to observe the formation of deep grooves or channels along the crystal boundaries on specimens exposed to prolonged heating *in vacuo*. The authors believe that this anticipation has also been verified.

Experiments have been made with six metals, viz. alu-

minium, antimony, cadmium, copper, silver, and zinc. The first three of these gave inconclusive results. Aluminium was found not to retain a bright metallic surface when heated in the highest available vacuum (about 0.002 millimetre); this metal was always found coated with a dark deposit, and the losses of weight observed were quite irregular, and usually very small, when the metal had not been melted. Antimony showed in several experiments a definite gain in weight, and otherwise behaved in an irregular manner; while in the case of cadmium tarnishing of the surface also occurred, and irregular results were obtained. In the case of copper, silver, and zinc, however, it was found possible to maintain the surfaces of the specimens perfectly clean and bright even after over forty hours' heating to a temperature about 100° C. below their respective melting points, and these metals yielded perfectly consistent results which are entirely in accord with the predictions of the authors based upon the hypothesis here described.

The specimens of metal in the two different conditions of crystallization were obtained in two ways. In the case of copper and silver they were obtained by casting direct; the specimens having the minute crystal structure were cast in metal moulds immersed in a freezing mixture so as to ensure the most rapid solidification possible, while the specimens having a very coarse structure were obtained by casting in moulds which were artificially heated and only allowed to cool slowly through the freezing point of the metal. In the case of zinc some difficulty was experienced in obtaining specimens having a sufficiently coarse structure in this way, owing to the severe oxidation which occurs in this metal when cooled very slowly in small masses. For that reason the method adopted was to roll down a small ingot of zinc into the form of a fairly thick sheet, and this sheet metal was then annealed in hydrogen until it had developed the desired coarse structure. The actual relative scales of crystal structure obtained in these ways is shown in photomicrographs Nos. 2, 3, 4, 5, 6, and 7, Plates XXIII. and XXIV., which represent two specimens typical of the coarse and fine-grained silver and zinc respectively.

Figs. 2 and 3, Plate XXIII., show the structure of the two

silver specimens, as cast, simply polished and lightly etched; the photograph of the "coarse" specimen shows portions of only three crystals in a field photographed under a magnification of only ten diameters. It was found, however, that these large crystals—probably as the result of the small amount of straining involved in the act of polishing—broke up into a number of somewhat smaller crystals, showing much twinning, as the result of prolonged heating *in vacuo*. The structure of the "coarse" specimen at the end of the operations is represented in Fig. 4, Plate XXIII., also under a magnification of ten diameters. The structure of the "fine" specimen was also modified in a similar manner, as shown by Fig. 5, Plate XXIV., but the ratio of crystal size in the two specimens is only very slightly affected by these changes. It should be mentioned that the photographs Nos. 4 and 5 (Plate XXIII.) represent the appearance of the specimens after heating *in vacuo* and *without any subsequent polishing or etching*. They are examples of the process of "vacuum etching" referred to in the later part of this paper.

The method of heating the specimens thus obtained was very simple; a small electric-resistance tube furnace was employed, the specimens being contained in a glazed porcelain tube, which was exhausted by means of a five-fall Sprengel pump provided with an automatic mercury lift, by means of which the exhaustion could be continued for many hours without attention. The temperatures were measured by means of platinum-platinum iridium thermocouples carefully calibrated, and the indications of these couples were measured by means of a Rosenhain-Melsom portable potentiometer. The two specimens of the same metal were in every case heated together, so that they were exposed to the same vacuum and as nearly as possible to the same temperature.

In the small furnace used for these experiments great uniformity of temperature could not be obtained; but, in order to obviate any risk of error from this cause, care was taken to place the specimens in the tube in such a way that the coarsely crystalline sample was in the hottest part of the tube nearest the centre of the furnace, while the finely-crystalline sample was kept in a position having a temperature by a few degrees

lower than that of the centre of the tube. These small temperature differences thus tended, if anything, to lessen rather than to accentuate the effect which the authors were seeking.

Periodical determinations of the pressure within the furnace were made by means of a McLeod gauge, and these observations showed that the first heating of a specimen which had not previously been heated *in vacuo* gave rise to the evolution of a considerable volume of gases; but the experimental evidence does not indicate that there is any marked difference between coarsely and finely crystalline samples of the same metal in this respect. During further or subsequent heatings, even when the specimens had been allowed to cool down to the ordinary temperature *in vacuo* and subjected to weighing, no such marked evolutions of gas occurred. The authors therefore decided to reject the results of the first heatings in every case owing to the possible error introduced by the removal of gases, although in actual fact these first observations also gave results entirely in accord with the authors' hypothesis. It should also be stated that the fact that the losses of weight were really due to volatilization of the metals was confirmed by the observation that films of the metal, and in some cases actual small crystals, were found condensed upon the colder portions of the furnace tube. These were removed carefully after each experiment, so as to avoid all risk of re-condensation upon the surfaces of the specimens. In the case of zinc, which was the first metal used for these experiments, this precaution was not always adopted, with the result that in one instance a slight gain of weight was found in one of the specimens.

Table I. gives the results of the weighings taken on two specimens of zinc after successive annealings *in vacuo*. The zinc employed for these experiments was derived from a batch presented to the Laboratory by Sir John Brunner for purposes of Alloys Research; it contains not less than 99.98 per cent. of zinc. The silver used for the experiments recorded in Tables II. and III. was purchased from Messrs. Johnson Matthey as 999 fine; while the copper used for the experiments described in Table IV. is electrolytic copper which has been re-melted and cast into ingot form.

TABLE I.—Zinc.

Coarsely Crystalline Specimen A.—Dimensions $2.7 \times 0.8 \times 0.075$ centimetres.

Superficial Area = 4.84 square centimetres. Weight = 1.1916 grammes.

Finely Crystalline Specimen B.—Dimensions $2.7 \times 0.8 \times 0.10$ centimetres.

Superficial Area = 5.02 square centimetres. Weight = 1.3071 grammes.

No. of Heat.	Duration.	Tempera- ture.	Loss in Weight of Coarsely Crystalline Specimen A.		Loss in Weight of Finely Crystalline Specimen B.		Ratio of Loss on B. and A.
			Actual Loss.	Loss per Sq. Cm.	Actual Loss.	Loss per Sq. Cm.	
	Hours.	Degrees C.	Gramme.	Gramme.	Gramme.	Gramme.	Per Sq. Cm.
1	2	280	0.0000	0.00000	0.0004	0.00008	...
2	5	310	0.0004	0.00008	0.0009	0.00018	2.25
3	2	370	0.0626	0.01300	0.1467	0.02950	2.26
*4	3	360	0.0003 (gain)	...	0.0006	0.00012	...
5	2	335	0.0008	0.00016	0.0019	0.00038	2.37

It will be seen that, apart from the first heating, which is rejected for reasons stated above, and heat No. 4, in which one of the specimens showed a slight gain of weight, the finely crystalline specimen showed a percentage loss, which remained slightly larger than twice that shown by the coarsely crystalline specimen.

The results of corresponding experiments with silver are shown in Table II.

Table II. contains the tabulated results of seven successive heatings of the same specimen of silver. Since the comparison specimens were approximately, but not accurately, of the same dimensions, the losses of weight have been expressed in grammes per square centimetre of the total superficial area of the specimen. Calculation in percentages of the weights of the specimens gives slightly different figures, but the ratio of loss between the two specimens is not materially altered. It will be seen that the results of heats Nos. 2, 3, 6, and 7 give very closely concordant results as regards the ratios of loss of the two specimens. The first heating gives a decidedly higher ratio, but this may be disregarded for reasons already stated. A somewhat similar consideration applies to heat

* Furnace not cleaned out between heats. Cf. results of heat 4.

No. 5, since during the heat previous to this the vacuum dropped, owing to breakage of the pump, during the final cooling. The specimen was thus able to absorb some gas during cooling, and we find an anomalously high loss at the next heat, while the two specimens show a percentage loss slightly higher in the coarse specimen. The fact that the presence of gases tends to disturb the proper ratio between the volatilization losses of the two specimens is further borne out by the results of heat No. 8. Here it was desired to continue the heat over a long period, and the apparatus was left running over-night. Unfortunately the pump broke down during the night, and the vacuum dropped somewhat (to a pressure of a few millimetres of mercury). The resulting losses of weight show a decidedly lower ratio of loss of B to loss of A than those of the four experiments which took an entirely undisturbed course.

TABLE II.—*Silver.*

Coarsely Crystalline Specimen A.—Dimensions $1.85 \times 0.775 \times 0.40$ centimetres.

Superficial Area= 4.96 square centimetres. Weight= 6.5541 grammes.

Finely Crystalline Specimen B.—Dimensions $1.35 \times 1.125 \times 0.40$ centimetres.

Superficial Area= 5.35 square centimetres. Weight= 6.9969 grammes.

No. of Heat.	Duration.	Tempera- ture.	Loss in Weight of Coarsely Crystalline Specimen A.		Loss in Weight of Finely Crystalline Specimen B.		Ratio of Loss on B. and A.
			Actual Loss.	Loss per Sq. Cm.	Actual Loss.	Loss per Sq. Cm.	
	Hours.	Degrees C.	Gramme.	Gramme.	Gramme.	Gramme.	Per Sq. Cm.
1	3.5	870	0.0294	0.0059	0.0553	0.0103	...
2	3.0	870	0.0255	0.0051	0.0329	0.0061	1.21
3	3.0	870	0.0321	0.0064	0.0433	0.0081	1.27
*5	5.0	870	0.2320	0.0466	0.2260	0.0422	...
6	5.0	870	0.0465	0.0093	0.0616	0.0115	1.24
7	5.5	870	0.0902	0.0182	0.1122	0.0210	1.16
†8	18.0	870	0.4451	0.0898	0.5157	0.0964	1.07

The results given in Table II. above have been confirmed by other series of heats; in every case the finely crystalline specimen was found to lose weight *in vacuo* at a greater rate

* Heat No. 5 follows a heat (not given above) during which pump broke down and vacuum dropped.

† Heat No. 8, pump broke down after about 18 hours' annealing, and vacuum dropped.

than the coarsely crystalline one, although, as might be anticipated, the actual ratio varied slightly with different specimens.

In order to test the question whether a similar phenomenon could be observed in the absence of a vacuum, two specimens of silver, also having coarse and fine structures, were heated for six hours in pure dry hydrogen at atmospheric pressure. It was found that the total rate of loss was very much smaller—about one-thousandth of that observed in heat 7 of Table II., but the ratio of the two specimens was over 3. As this was an isolated experiment, the authors do not attach much importance to it; but its indications, so far as they go, are interesting as suggesting that the volatilization of the coarsely crystalline metal is more considerably hindered by the presence of hydrogen than that of the finely crystalline specimen, while the small total loss of weight also indicates that the larger losses observed *in vacuo* are really due to loss of metal, and not to removal of oxygen gas, since this gas would have been most effectively removed in an atmosphere of hydrogen.

Table III. records the results of the second and third heats carried out on two specimens of copper, again of approximately similar dimensions, and having a coarse and fine crystal structure respectively.

TABLE III.—Copper.

Coarsely Crystalline Specimen A.—Dimensions $1.50 \times 0.85 \times 0.45$ centimetres.

Superficial Area = 4.665 square centimetres. Weight = 4.2942 grammes.*

Finely Crystalline Specimen B.—Dimensions $1.45 \times 0.95 \times 0.375$ centimetres.

Superficial Area = 4.554 square centimetres. Weight = 4.8302 grammes.

No. of Heat.	Duration.	Temperature.	Loss in Weight of Coarsely Crystalline Specimen A.		Loss in Weight of Finely Crystalline Specimen B.		Ratio of Loss on B. and A.
			Actual Loss.	Loss per Sq. Cm.	Actual Loss.	Loss per Sq. Cm.	
1	Hours. 3	Degrees C. 950
2	3	1015	0.0076	0.0016	0.0114	0.0025	1.56
3	4	1015	0.0150	0.0032	0.0192	0.0042	1.31

* This specimen contains two blow-holes, and is therefore apparently lighter than its dimensions would indicate.

These figures confirm the results obtained with zinc and silver, although the actual losses of weight are much smaller—as might be anticipated from the known lower volatility of copper. The ratio of the losses is again between 1·3 and 1·5, so that all three metals give results of the same order of magnitude, although naturally differing in regard to actual values found.

Taken together, the results given in the three tables above, and confirmed by other determinations not quoted in detail, appear to the authors to furnish a very clear experimental demonstration of the anticipation derived from their hypothesis, and thus to lend some weight to the probability of that hypothesis itself.

The microscopic examination of the specimens which have been exposed to prolonged heating *in vacuo* offers several points of interest which also bear upon the authors' hypothesis. In the first place a phenomenon, which may be called "vacuum etching," is observed—most favourably in the case of silver. A smooth polished specimen, after heating in a high vacuum to a high temperature exhibits a beautifully etched surface, showing very clearly the actual structure of the metal.

Examples of such vacuum etching have already been given in Figs. 4 and 5, Plate XXIII., and a further example is shown in Fig. 8, Plate XXV., which shows the entire surface of a specimen of silver magnified 3 diameters. A few hours' exposure to heat *in vacuo* is sufficient to develop such etching; if the exposure is prolonged, the "etching" becomes deeper and rougher—a fact which is incidentally illustrated by Figs. 10 and 11, Plate XXVI., taken under higher magnification. Similar phenomena of vacuum etching have also been observed in copper, antimony, nickel and iron. In the case of silver a similar process of "etching" has also been observed in certain instances when the metal is heated in air; an example of this kind, relating to a previously strained specimen in which multiple twinning has developed, is shown in Fig. 9, Plate XXV. This action has also been observed when platinum is heated in air ⁽¹⁵⁾.

The phenomenon in question is probably a double one;

PLATE XXIII

SILVER.

Before Annealing.



FIG. 2.—Coarse Structure.
Magnified 10 diameters.

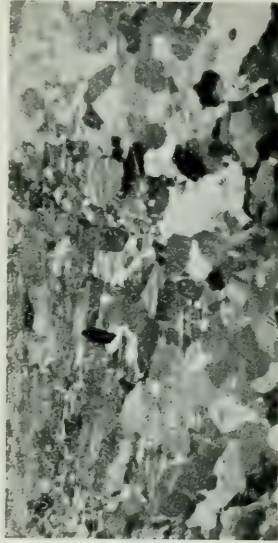


FIG. 3.—Fine Structure.
Magnified 10 diameters.

After Annealing.



FIG. 4.—Coarse Structure.
Magnified 10 diameters.

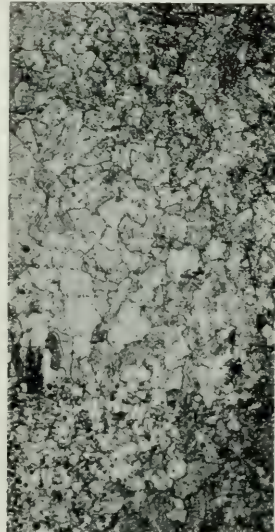


FIG. 5.—Fine Structure.
Magnified 10 diameters.

(Oblique illumination.)

PLATE XXIV

ZINC.

Before Annealing.

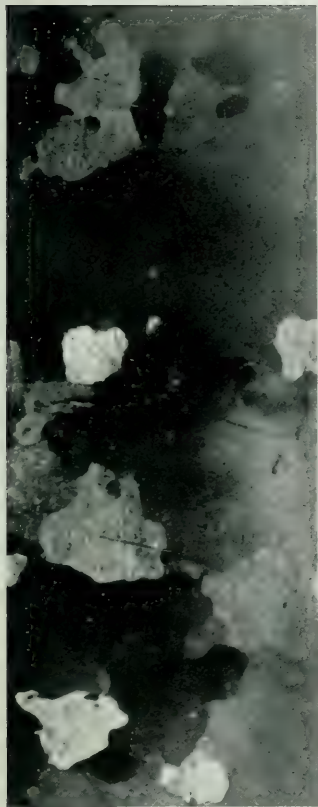


FIG. 6.—Coarse Structure.
Magnified 10 diameters.

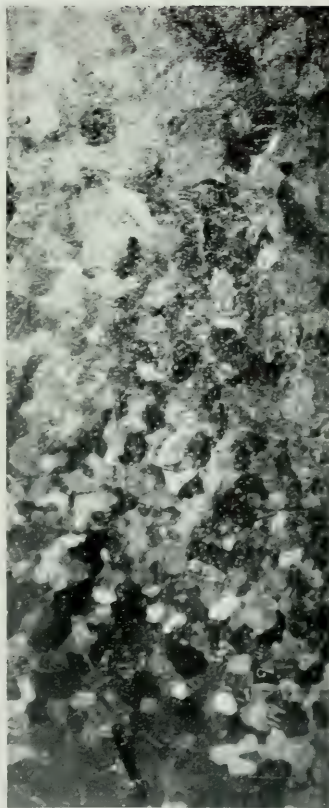
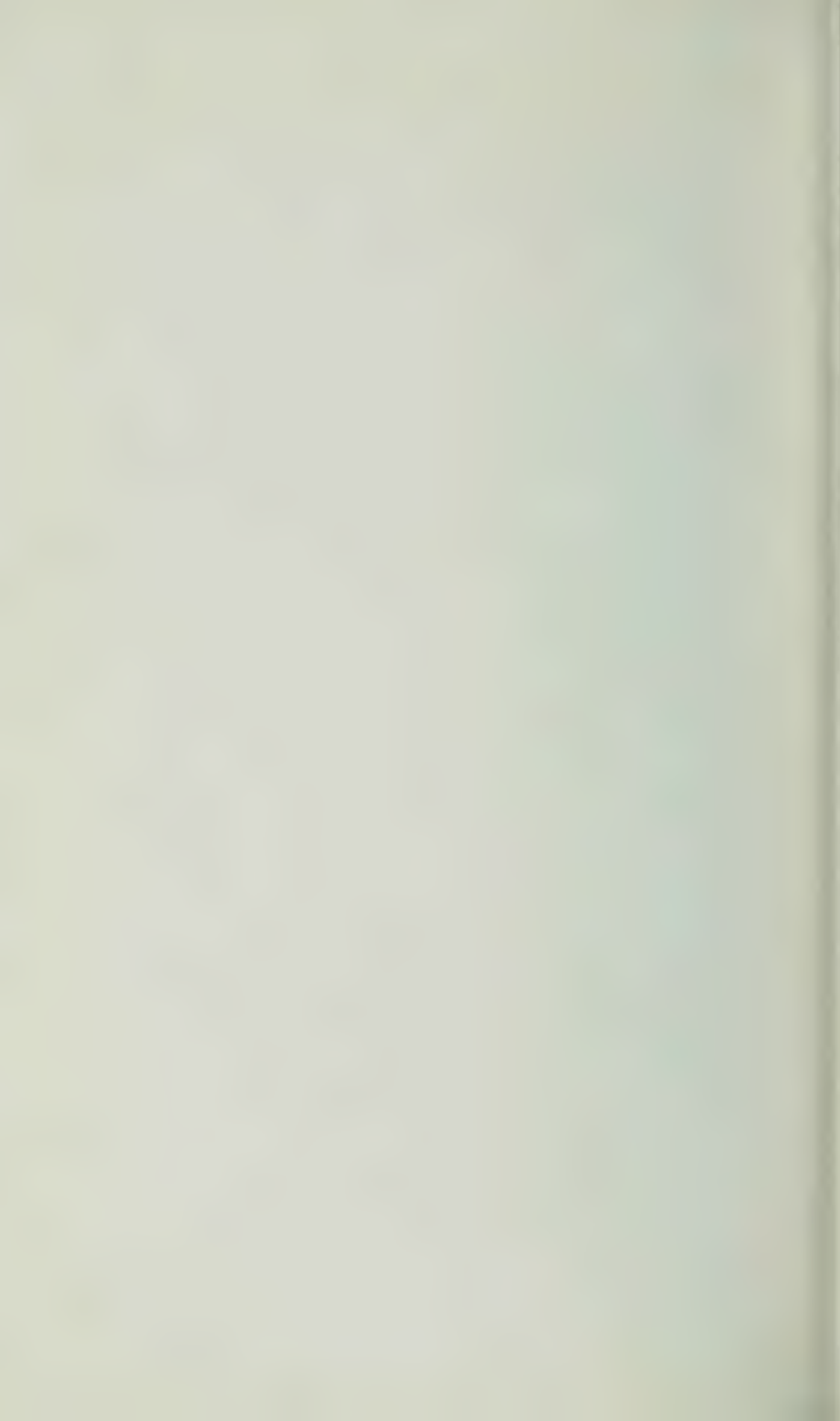


FIG. 7.—Fine Structure.
Magnified 10 diameters.

(Oblique illumination.)



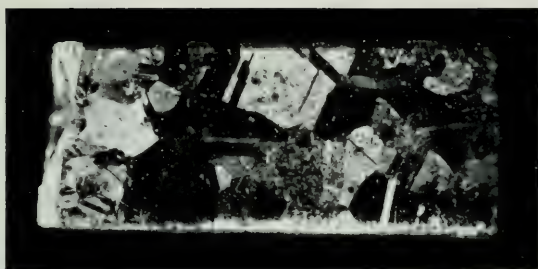
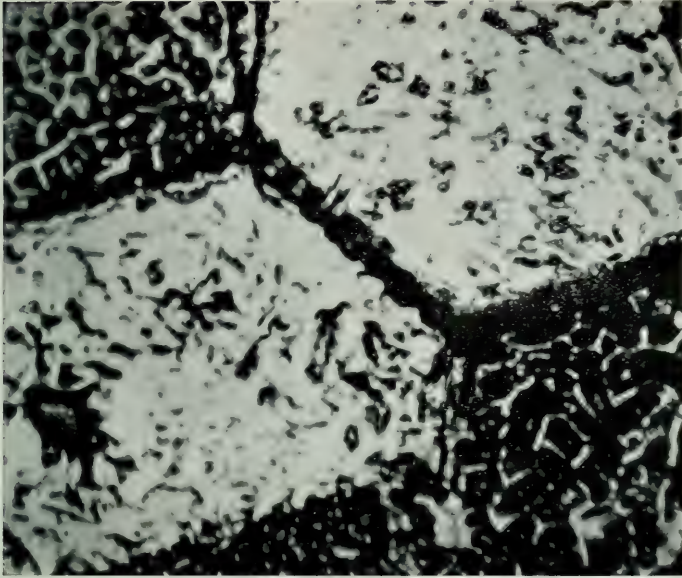


FIG. 8.—Silver annealed *in vacuo*. Magnified 3 diameters.
(*Oblique illumination.*)



FIG. 9.—Silver annealed in Air. Magnified 300 diameters.
(*Vertical illumination.*)



T

FIG. 10.—Coarse Structure Silver. Magnified 150 diameters.



FIG. 11.—Coarse Structure Zinc. Magnified 150 diameters.
(*Vertical illumination.*)

it appears partly to arise from a slight loss of metal from the surface by direct volatilization—a process which would act very much like an attack with a solvent which leaves no residue. In addition to this action—which would only be pronounced in a high vacuum, there is probably also a surface change due to the crystallization of the surface amorphous film produced by polishing. It would seem that under the combined influence of a high temperature and the removal of atmospheric pressure, the surface layer may re-arrange itself in conformity with the crystalline arrangement beneath, thus giving rise to surface facets exactly similar to those which might be produced by etching or evaporation. That this latter action is not solely responsible for the phenomenon, however, is proved by the fact that an etched specimen which is heated in such a manner as to undergo recrystallization while in the vacuum exhibits the newly-found structure by “vacuum etching”⁽¹⁶⁾.

Specimens, particularly of silver, which have been exposed to somewhat prolonged heating *in vacuo*, also exhibit interesting microscopic features at the junction of crystals. The boundaries appear as more or less deep and narrow grooves or channels, on the sides of which the orientations of the two crystals can be traced.

Photographs of these channels seen under a magnification of 150 diameters are shown in Figs. 10 and 11, Plate XXVI., which relate to silver and zinc respectively. That, on the authors' hypothesis, the formation of such grooves or channels was to be anticipated has already been indicated, but a further interesting observation remains to be recorded. The specimens of silver employed by the authors frequently showed extremely well-developed twinning, so that the surface of the specimen was divided not only by intercrystalline boundaries in the ordinary sense, but also by a number of boundaries between adjacent twin crystals. It is interesting to find, however, that on the specimens which have been heated *in vacuo*, while the ordinary crystal boundaries show the deep grooves or channels mentioned above, the boundaries between twin crystals show no groove or channel whatever. A twin boundary without a channel appears in Fig. 10, Plate XXVI., terminating near

the bottom left-hand corner of the photomicrograph. This is entirely in accordance with the authors' views, since in a twin boundary there is no interruption of crystalline orientation, and therefore no room for the interposition of any amorphous cementing material. The formation of the grooves or channels at the crystal boundaries themselves is thus shown to be due to some special cause residing in those boundaries themselves, and is not an effect due to the mere juxtaposition of two areas of differing crystalline orientation. This latter description applies quite strictly to the differences of level produced by etching, since differences of level are frequently produced by etching in the case of twin boundaries. This observation, therefore, constitutes another fact capable of ready explanation by the aid of the authors' hypothesis.

In conclusion, while the authors do not claim to have brought forward a conclusive proof of the existence of an intercrystalline amorphous cement in metals, they consider that they have brought forward a number of facts which require special explanation. The hypothesis of an amorphous intercrystalline cement appears to afford such an explanation in a simple manner, and this hypothesis has led the authors to make certain further deductions capable of experimental test. The results of these experimental tests are described in the paper, and the authors regard them as strongly confirming their deductions. They, therefore, regard the conception of an amorphous intercrystalline cement as established on a basis which entitles them to look upon it as rather more than a mere working hypothesis, and to hope that future research may open up a means for establishing their theory on a more complete basis of experimental fact.

The experiments described in this paper have been carried out in the Metallurgical Laboratory of the National Physical Laboratory, and the authors desire to express their thanks to the Director for his interest in the matter.

APPENDIX.

THE FORMATION OF TWINNED CRYSTALS IN SILVER.

The origin of twinned crystals in metals has been the subject of considerable discussion, and as the experiments on the prolonged annealing of silver in various conditions which have been undertaken in connection with the present research appear to throw some light on the question, it is proposed to refer to them here. In the experiments with cast silver it was found that twin crystals, extending right through a mass several millimetres thick, were developed after heating either in air or *in vacuo*. The existence of this structure was in some cases revealed by "vacuum etching," while in other cases re-polishing and etching after annealing was required. In order to ascertain whether the formation of these twinned crystals in cast metal, which had never been subjected to intentional strain, might be ascribed to the strains set up by the polishing process, the following experiment was tried: Two small pieces of silver were cast from the same melt; on one of these (A) a surface was polished and etched with nitric acid, while the other (B) was etched with nitric acid without any previous polishing whatever. At this stage both showed a crystalline structure quite free from twinning. Both were then heated for two hours at 780°C . *in vacuo*. On removal from the furnace, specimen A, which had previously been polished, showed distinct twinning in places as revealed by vacuum etching; while specimen B showed no signs of twinning. Both were then polished and again etched, when A was found to be very largely twinned; while B still showed no twinning. In other observations it was found that either a saw-cut, where the specimen had been cut off, or blow-holes in the castings gave rise to some twinning in their neighbourhood. These experiments clearly indicate that twinning takes place during annealing provided that the metal has previously been strained, although such strain may be slight and local. Where such strain is small, as in simple polishing, the twinning is not mechanical, but is only developed during the annealing process after strain.

It is interesting to note that zinc treated in the same manner, which led to vigorous twinning in silver, showed no signs of twinning. This fact is probably connected with the circumstance that zinc is one of those metals which do not crystallize in the regular system.

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DISCUSSION.

Dr. C. H. DESCH (Glasgow), in opening the discussion, said he desired to offer one or two criticisms on the paper. The hypothesis put forward was certainly a very pretty one, and seemed to account for the facts very well. But it was necessary to put it to certain tests before it could be accepted as valid. There were difficulties in assuming the presence of the amorphous intercrystalline material, but those difficulties could be overcome if good evidence were brought forward for the existence of the film. In the diagram on p. 156 the amorphous crystalline material was represented as that which was left over after the crystal units had arranged themselves. The question arose, What was the size of a crystal unit in the case of a metal? All the evidence went to show that the molecular conditions of solid metals were very simple—that the molecules consisted of one or a very few atoms. The case of water was quoted, but even in water the complexity was not very great, only $3\text{H}_2\text{O}$. One would, therefore, expect the intercrystalline layer, if due to such a cause, to be extremely thin. The experiments furnished some means of calculating what the thickness must be if the results observed by the authors were to be explained on that assumption. He had gone about the matter in the following way. He had calculated for the coarse and fine specimens of silver shown on Plate XXXIII. the approximate area of the intercrystalline boundaries; he had taken the crystals to be cubes, and had measured their average size. He had calculated the total area of the intercrystalline boundaries; then he had taken the difference between the loss in a single experiment on heating the coarse and fine specimens *in vacuo* as representing material which came from the intercrystalline boundary. Then one could calculate the volume of the metal lost, and knowing the area of the intercrystalline boundaries it was possible to calculate the thickness of the boundaries. That was a very rough way of making a calculation. He found that the boundaries must be at least several thousand molecules thick, and he did not think that a layer of anything like that thickness could be produced merely from matter left over from the formation of the crystal units. Then they were met with the fact that, the experiments being undoubtedly correct, there was a difference between the amount of vapour given off by a coarse and a fine crystallized metal; but that result might be explained without assuming an amorphous intercrystalline layer. The vapour pressure was greater on a small crystal than on a larger one of the same substance. That had been proved thermodynamically, and shown experimentally for organic substances by Pavloff. Although the matter had not been decided in the case of metals, he saw no reason to suppose that it would not be the case—that the smaller crystals would have a higher vapour pressure than the large ones. For those reasons he did not feel able to accept the authors' explanation,

although he admitted that what he had said did not disprove the existence of an amorphous intercrystalline layer. Turning to the Appendix, there was little to object to in it, except perhaps the statement at the end, that twinning would be less likely to occur in one of those metals which did not crystallize in the regular system. That seemed to him rather open to question. For instance, in the case of a mineral with many feldspars, it was the triclinic feldspars, those of lower symmetry, which showed the development of twinning most readily. In conclusion, he wished to congratulate the authors on the very excellent photograph shown on Plate XXV., Fig. 9, which was in itself a lesson in the crystallography of metallic substances.

MR. SYDNEY W. SMITH, B.Sc., Assoc.R.S.M. (London), said he would confine his remarks to the case of silver with which the authors had dealt. On page 159, where the authors began to describe their work, the statement appeared: "It may be mentioned that the authors' interest in the present subject was first evoked by the observation of the striking fact that a specimen of such an extremely ductile metal as pure silver can be made brittle by continued heating *in vacuo*." It was implied by that statement that the result of heating pure silver *in vacuo* was to make it brittle. The authors did not say, however, in the course of their paper whether the two specimens upon which they based their results showed brittleness after the continued treatment *in vacuo* to which they were subjected, and he thought that if it had been so, it would have been a fact which they would have recorded. There were other conditions under which pure silver might be brittle (apart altogether from the presence of impurities), without the necessity of heating it *in vacuo*. Then with regard to the preparation of the specimens. The finely crystallized specimens were prepared by casting in a chilled mould, and the others were slowly cooled. Did the authors compare the densities of those two specimens prepared in that way, because there was likely to be a considerable difference in the density of chilled silver and slowly cooled silver. That of the chilled silver was likely to be much lower than that of the slowly cooled silver, for the simple reason that in the former case the occluded gases had not the same opportunity of escaping as they had in the latter. Taking the density of silver at 10.5, the chilled silver might well show as low a density as 8.7, while slowly cooled silver might be as low as 9.4. The authors had evidently encountered the presence of occluded gases in their experiments, because they had adopted the course of neglecting all first heatings. There was an inconsistency in their remarks on that point. They said (on page 164), in speaking of the evolution of gases: "The experimental evidence does not indicate that there is any marked difference between coarsely and finely crystalline samples of the same metal in this respect"; but on page 166, in the table given, the first weights enumerated showed that they actually lost nearly twice as much in the case of the finely crystalline specimen. That, of course, was in accordance with what he had already said about the difference in the amount of gas occluded. He did not wish to labour the

question of occluded gases, because he did not think it affected in any way the interpretation which the authors would put upon their results. There was another matter, however, to which he wished to draw attention, because he thought it was of considerable importance. The authors had been at great pains in showing the small differences of loss in weight due to volatilization. He thought they would have found that far more striking results would have been furnished if they had merely experimented with the action of cold nitric acid on samples of prepared silver. If two buttons of silver, one of which had been slowly cooled and the other rapidly cooled, were put into cold nitric acid, not only was the rate of loss of weight of one greater than the other, but in the course of time the chilled one disappeared altogether—having completely dissolved—long before the other had approached anything like complete solution. The state of the metal under those two conditions was such that in one case it was able to dissolve more readily than in the other, and he was quite unable to see that the authors had done any more than show that a similar property held good in the case of volatilization. They had found that the chilled specimen volatilized more readily than the slowly cooled one. If they had continued their volatilizations to a point nearer the melting point they would probably have found still greater differences. The authors did not claim that the whole of the losses given in the tables were due to the volatilization of the intercrystalline amorphous layer, but he was quite unable to see that they could justly discriminate between the one and the other. He thought they had merely shown that the specimens prepared under those two different conditions volatilized at different rates.

Dr. T. K. ROSE (London) said that, like Dr. Desch, he had made a little calculation based on the results of the experiments made by the authors on the zinc specimens. According to his calculation, the details of which he had given to the authors, the more volatile amorphous constituent must be 200 times more volatile than the other one in these experiments, the result being that the space between the crystals would be hollowed out to a depth of 5 millimetres, the thickness of the specimens being only 1 millimetre.

Professor H. C. H. CARPENTER, M.A., Ph.D. (Vice-President), said he was sure all those present regretted the absence not only of Dr. Bengough but of Dr. Beilby, whose work was so copiously quoted in the paper. He hoped those two gentlemen would be able to contribute to the written discussion. In the first place, he desired to refer to one or two small points in the paper before coming to the authors' main thesis. In Table II. on page 166 he wished to draw attention to heats Nos. 6 and 7, dealing with the rate of volatilization of silver. There the duration of heating was nearly the same, viz. 5.0 and 5.5 hours respectively; the temperature was the same, but the loss of weight both in the coarsely and finely crystalline specimen was almost double in No. 7 what it was in No. 6. He wished to ask the authors if they could give an explana-

tion of that. He did not say it was a discrepancy, but he certainly thought it required explanation. Nobody had yet drawn attention to the fact that the authors had introduced what was practically a new method of etching specimens, and an extremely valuable one. He thought members should recognise that "vacuum etching" was a very important new method of developing crystalline structures. He wished to ask the authors whether they had any special reason for not including any photomicrographs of copper. They gave the results they obtained with silver and zinc; but he thought that as most of the members were acquainted with copper, it would have been interesting to have seen the results of the effect of volatilization on the copper specimens at the temperatures quoted. He also wished to ask whether in their copper specimens they noticed any signs of oxide. The specimens were obtained by casting, and he did not know of any method of casting copper so as to obtain it without oxide. He would like to know whether they noticed any evidence of oxide in between the copper crystals, and exactly what form it took. The authors had been deservedly complimented on Fig. 9 on Plate XXV., which was one of the most striking photographs he had ever seen. It was interesting because there appeared to have been in that case a selective evaporation from the entire crystal which was absent from any of the neighbouring crystals. He would like to know whether that was an isolated case, or whether other instances were noticed, because it was rather different from the volatilization of the metal from the boundaries.

Dr. ROSENHAIN said that it was heated in air.

Professor CARPENTER replied that volatilization occurred.

Dr. ROSENHAIN replied that that was always the case.

Professor CARPENTER, continuing, said that the authors had dealt with the bearing of the presence of eutectics on their theory rather too briefly. He thought that question was worthy of fuller treatment because Quincke's theory of the foam-cell structure of metals assumed that even in the purest specimens there was sufficient impurity to form a eutectic. In that connection he thought it was a pity that the authors, at any rate in the case of silver, did not work with by any means as pure a metal as it was possible to get. The purity of the silver was quoted at 999, whereas it could be obtained 10.000 pure; *i.e.* fully ten times the purity of the silver with which the authors dealt. Where it was a question of deciding whether or not a eutectic had any influence it was very important to work with as pure a metal as possible. Perhaps the authors would extend their observations on silver etching *in vacuo* to silver of that degree of purity. Another point which had not been touched upon arose out of the paper. He would assume for the moment, what none of the other speakers had done, that the authors' hypothesis was established, and would consider in its light the question of diffusion. If their view was correct then there were no such thing as exclusively solid

diffusion in any metal. Taking a copper-zinc alloy of 70 30 composition which exhibited "cores" in the freshly cast condition, on annealing that specimen to equilibrium, if the authors' hypothesis was correct, that could only take place by the transport of the molecules from one crystal through the cement which was liquid, or virtually liquid, to another crystal. That was to say, in the diffusion both liquid and solid phases necessarily participated. That seemed to him to be the logical issue of that hypothesis as applied to solid solutions. The point he wished to make was *that it was exactly the same conclusion that Mr. Edwards came to a year ago in the discussion on solid solutions in answer to an objection raised by Dr. Rosenhain.* Dr. Rosenhain had stated that if Mr. Edwards' theory was correct then he must assume that crystals containing hundreds of thousands of molecules could diffuse *in toto* through a crystalline solid, and Mr. Edwards was driven to the above deduction, which was exactly the same conclusion as appeared to follow from the authors' hypothesis. That, he thought, was very interesting, because it showed how entirely different lines of thought, which were apparently antagonistic, had led to the same conclusion.

Dr. WALTER ROSENHAIN said he had a very great deal to reply to, because the criticisms which had been levelled against the paper were very useful and interesting. The discussion that had occurred was just the kind of discussion that was required on such a paper. He did not say that he agreed with the opinions that had been expressed by the various speakers, but they were certainly interesting and suggestive. First of all, both Dr. Desch and Dr. Rose had exercised their mathematical faculties in making very pretty calculations. Those calculations, or similar ones, he (Dr. Rosenhain) had also made; and, as would be seen in the paper, he recognized the fact that the *whole* of the difference in the volatilization losses of the two things could not be due to amorphous matter from the boundaries. It must be remembered that while it might be true that isolated crystals of different sizes would have different vapour pressures, he did not think it would follow that an aggregate consisting of small crystals would have a different vapour pressure from an aggregate consisting of large crystals. That was a totally different matter; it was a question of the amount of surface exposed. A start had to be made, therefore, under conditions in which any difference of vapour pressure between the two might be regarded as being essentially a difference which must be due to some special cause other than the size of the crystals. But when the volatilization had gone on for a certain length of time, then channels began to develop between the crystals, and thus the area over which evaporation could take place rapidly increased. That area was increasing enormously more rapidly in the early stages in the finely crystallized specimens than in the coarsely crystallized specimens, and consequently the further evaporation would go on not only from the amorphous boundary material, which must necessarily be very thin, but also from the sides and the interior faces of the crystals. If that hypothesis was correct, if channels or spaces were being opened up between the crystals by the process of evaporating out the cement, in that way a

path would be opened out for further volatilization to a greater extent from the finely crystalline aggregate than from the coarsely crystalline aggregate; in fact, the two things would be reduced to the level which Dr. Desch referred to, of a loose mass of large crystals and a loose mass of small ones.

The authors had found that in the great majority of specimens heated *in vacuo* the silver became brittle to the extent that when it was pulled out in tension the breaking followed the boundaries of the crystals, whereas before it would not have followed those boundaries. He was not prepared to admit that the crystal unit of a metal was as small as Dr. Desch submitted. The evidence that gentleman quoted was of a very indirect and inconclusive kind as regards solid metals. It was known that liquid metal was probably of a simple atomic constitution, but he did not know of any conclusive evidence as to the solid metal. Even then it did not follow that the physico-chemical molecule was necessarily the crystal molecule. He assumed it was for the moment, for simplicity of argument in the paper, but it might not be. A physico-chemical unit might exist which might be many hundreds of molecules in dimension.

With regard to the experiment of powdering a substance and finding it had a higher vapour pressure than before, that was again simply a function of the amorphous phase. Not only had a large quantity of amorphous matter been produced, but if that amorphous matter was more volatile, as he had reason to believe it must be, then the result was explained from that cause alone.

In reply to Mr. Smith's remarks, he wished to say that the heating of silver *in vacuo* to make it brittle was an interesting experiment which he could easily try for himself. It did not invariably succeed, but the success did not depend upon the question of impurities. There was no sufficient amount of impurity in any single specimen of silver used in the experiments to account for the degree of brittleness found in some cases. The experiment Mr. Smith described in regard to the action of nitric acid was a very interesting confirmation of the authors' results: it was exactly what they expected from their hypothesis. If Mr. Smith watered down the authors' conclusions by saying that they had merely proved that the condition of the metal when it was finely crystallized was such as to favour volatilization, whereas the condition of the metal when it was in large crystals did not favour volatilization, that was merely putting in vague language what the authors had tried to put into a precise and useful form.

Professor Carpenter had asked one or two questions to which he would reply very briefly. There was a limit to the number of illustrations with which it was possible to burden the paper; but the appearance of the copper when it was heated in that way was exactly like copper etched with acid ferric chloride. The copper used by the authors undoubtedly contained oxygen. It was not the oxide that disappeared on heating *in vacuo*; it simply etched the crystal boundaries; in fact, the authors found that practically every metal which could be preserved in a bright condition was etched on the surface in that way. With regard to the question of

selective evaporation concerning Fig. 9, Plate XXV., one had to bear in mind what happened in that case when a piece of silver was heated in air. An apparent etching action, which was partly volatilization and partly surface recrystallization, generally took place over certain portions of the specimen only. The one the authors had chosen happened to be surrounded by other crystals which were not so deeply etched; whereas a little way away it would be found that the whole mass was etched in that way. He could only say in conclusion that the authors did not claim in the paper that they had finally proved their hypothesis; but he thought that, in spite of the illuminating criticism which had been expressed on it, there was still every reason to say that the hypothesis was sufficiently well established to deserve a great deal of further consideration.

The PRESIDENT said he thought the author and his co-worker were to be congratulated on the extremely clear and lucid manner in which they had dealt with a very abstruse subject, and that they deserved a hearty vote of thanks for their labours, which vote he had pleasure in proposing. He had also pleasure in proposing a vote of thanks to Dr. G. T. Beilby, F.R.S., for his paper on "The Solidification of Metals from the Liquid State," which, in Dr. Beilby's absence, would be taken as read. The resolution of thanks to Dr. Rosenhain, Mr. Ewen, and Dr. Beilby was then put and carried unanimously.

COMMUNICATIONS.

Dr. G. D. BENGOUGH, M.A. (Liverpool), wrote that he was very glad that Dr. Rosenhain had carried out the intention he had foreshadowed in discussing his (Dr. Bengough's) paper at the Annual General Meeting in January 1912,* and had published his work on intercrystalline cement in metals.

He agreed with the authors in their statement on p. 156, that "upon the strength and integrity of this amorphous cement the strength of the metal will largely depend." He had himself stated that view even more emphatically in the following words: "The unstable vitreous amorphous material of Beilby plays a far more fundamental part in determining the mechanical properties of metals and alloys than has hitherto been suspected. The industrial alloys of copper, and even copper itself, depend for their commercially useful properties entirely upon this cement." He had arrived at his conclusions indirectly by a process of reasoning from the results of his mechanical tests. To the present authors belonged the credit of producing the first direct experimental evidence of its existence. The work must have been immensely difficult, but it had evidently been carried out with a very high order of accuracy. He congratulated the authors both on the reasoning, which had suggested the work, and on the work itself.

* *Journal of the Institute of Metals*, No. 1, 1912, vol. vii. p. 178.

The authors' view differed from those which he had himself put forward at the January 1912 Meeting of the Institute in the matter of the stability of the cement at high temperatures.* The authors considered that it could exist after reheating to temperatures within 100° C. of the melting points of several metals, whereas he had suggested that—in the case of copper, for instance—it recrystallized after reheating to about 400° C. below the melting point. They also objected to his suggestion that the cement might be the result of counter-attractions of surrounding crystals, on the ground that the cement would be unstable. He was not concerned to defend his original suggestion, as he thought the authors' view was an improvement on it, but he was by no means sure that the cement formed in the way they suggested could be considered stable. At high temperatures might not these transition products have a tendency to diffuse towards one another and form themselves into units capable of fitting into the crystal structure whenever an opportunity were afforded by recrystallization following work?

In some cases the mechanical properties of metals at high temperatures could be best explained on the authors' view that the cement persisted up to temperatures in the neighbourhood of the melting point. For instance, a certain special brass which he had examined pulled out to a fine point, just like glass would do, having an enormous elongation. In other cases, especially with cast metals, this did not happen at all; the elongation was low, and numerous cracks developed in the brass at varying distances from the point of fracture. He had thought this to be due to the disappearance of the cement, and the occurrence of true intercrystalline fracture. There was, of course, the possibility that in the case of comparatively impure cast metals the cement persisted instead of disappearing, but lost its ductility at temperatures a good deal below the melting point, owing to the presence of traces of impurity—as, for instance, in the case of cast brass A in the paper already mentioned.

On the whole he thought that the mechanical properties of the metals and single-phase alloys, which he had hitherto examined at high temperatures, could be explained rather better by the authors' idea of the persistence of the cement to the neighbourhood of the melting point and its softening than by his own suggestions. He was, however, carrying out some rather crucial experiments on the matter, which he would hope to report in due course.

Professor HENRY M. HOWE (Columbia University, U.S.A.) wrote that on the authors' wholly reasonable theory rupture ought, in a considerable proportion of cases, to run close beside the crystal boundaries.

The rupture must follow the path of least resistance under the existing conditions, yet in so heterogeneous and granitic a body as steel, made up of particles of different substances very unlike in their physical properties, modulus of elasticity, cohesion, plasticity, &c., great apparent capriciousness was to be expected, and even in pure metals con-

* *Journal of the Institute of Metals*, No. 1, 1912, vol. vii. p. 172.

siderable caprice was to be expected. The path which rupture followed on emerging from a given crystal and encountering its neighbour depended on a great variety of local conditions, such as the inclination of the existing cleavages of that near to the stress. But as, in spite of that capriciousness, rupture habitually avoided the crystal boundaries and passed through the crystals themselves, the authors' inference that the boundaries themselves were stronger than the crystals which they bound was just; indeed, in view of the inherent tendency to caprice, the regularity with which rupture avoided the boundaries indicated that those boundaries were not only strong but much stronger than the crystals.

But, on the authors' theory that the extra strength of the boundaries was due to their amorphousness, there was nothing to prevent rupture, in its passage across the crystals, from travelling close along beside the boundaries. The extra strength of the amorphous matter in the boundaries would not strengthen the adjoining part of the crystals in immediate contact with those boundaries.

To make that a little clearer, let it be taken that abutting against the assumed amorphous boundary filling was the parietal surface of the crystal proper, the surface on one side of which was amorphous boundary filling, and on the other side of which was the marginal true crystalline matter. The theory that the boundary filling was strengthened by being amorphous, and thus resisted rupture, did not imply that the marginal crystalline matter was in any way stronger than the rest of the crystal. And if it were no stronger, then rupture would travel as freely through that marginal region of the crystal as along any other path. But the probability was that, in a certain proportion of cases, the path of greatest stress lay in a crystal close to and along its boundary. Hence in that proportion of cases rupture should travel through the marginal matter close to the crystal boundary.

In brief, while the authors' theory explained readily why rupture should avoid the boundary filling proper, it did not explain why it should avoid the marginal matter of the crystal in immediate contact with that boundary.

Hence, in order to test the theory, it should be closely observed whether the path which rupture avoided was strictly and solely the boundary filling, or whether it included also the marginal matter; for in the latter case the authors' theory would need some extension in order to explain that avoidance.

It was true that the rupture of two well-glued pieces of wood habitually avoided the marginal part of the wood. But there the cleavage of the wood was so powerful in determining the path of rupture that rupture would be expected to pass close alongside the glue for only a very minute distance; and indeed the glue might well impregnate so porous a material as wood for an appreciable distance, and so strengthen the marginal matter.

Dr. ROSENHAIN wrote, in further reply to the discussion, that he wished to reply a little more fully, particularly to Professor Carpenter's

remarks, than had been possible in the strictly limited verbal discussion. Professor Carpenter had raised the point whether it was sufficient to dismiss the question of possible minute traces of eutectics in slightly impure metals as summarily as had been done by the authors of the paper. Taking as an example some of the silver used in the present research, having impurities of the order of 0.1 per cent., it was pretty evident from our present knowledge of the constitution of alloys that no eutectic could be present in the crystal boundaries, at all events after the metal had been annealed for some time at an elevated temperature. It was, in fact, not only a deduction from all accurate investigations of alloys, but also a definite requirement of thermodynamics that there must be a slight solubility in the solid state between any two metals. In most of the accurately studied cases solid solubilities of considerable magnitude had been found. Consequently he (Dr. Rosenhain) thought that any theory—such as that of Quincke's foam cells—which relied upon the formation of eutectics in metals containing only traces of impurities must break down on that ground alone.

Next, as regards the question of diffusion in solid metals. If he had understood Professor Carpenter correctly, his idea was that if there was such an amorphous intercrystalline cement this substance would be the seat of all metallic diffusion, so that such diffusion would occur in what was really undercooled liquid and not in the true crystalline solid. This might perhaps be the case in a homogeneous metal or alloy into which another metal was diffusing, as in some cementation processes, &c. But the example quoted by Professor Carpenter was surely a little unfortunate, since the removal of "cores" from the microstructures of solid solutions by subsequent annealing could not take place by way of the boundary cement. These cores were due, as a rule, not to the juxtaposition of various crystals of different composition, but to a variation of composition within the boundaries of an individual crystal. This was apparent from the microstructures seen in many cast specimens of solid-solution alloys, such as copper-zinc and zinc-aluminium. Now if the amorphous cement was of the character assumed by the theory which Mr. Ewen and he had advanced, then it existed only in the boundaries between such crystals and not at all in the boundaries, which were almost always more or less vague and ill-defined, between the regions of different concentration within a single crystal of a solid solution. Therefore, when these variations of concentration were equalised on annealing, that implied a diffusion of the dissolved metal within the mass of each individual crystal, and the aid of the amorphous cement could hardly be invoked in such a case. The objection which he (Dr. Rosenhain) had raised to the theory of Mr. Edwards, referred to by Professor Carpenter, therefore still held good.

In reply to Dr. Bengough's communication Dr. Rosenhain wished to express his pleasure at that gentleman's cordial support of the views put forward in the present paper. The authors of the paper had been anxious to advance no claims which could in any way infringe upon Dr. Bengough's priority of publication in regard to the amorphous cement theory, and they were therefore glad that Dr. Bengough had quoted in

full what was from this point of view the most important sentence in his paper on this subject.

With regard to the stability of the cement, there could be no doubt that at temperatures below the solidus all amorphous metal, however produced, must be essentially metastable. Recently Tammann had gone so far as to reject the whole conception of the existence of an amorphous phase, principally on the ground that it was contrary to the phase rule. In doing this, Tammann had made the mistake of applying the phase rule to what was acknowledged to be an unstable, or metastable system, so that his argument was quite without weight. There was further no doubt that as the temperature was raised the tendency of the metastable amorphous metal to revert to the stable crystalline phase would increase, at all events until temperatures very close to the melting point were attained, but the point which the present authors desired to make was that this tendency to crystallize could not come into play except where there was room for the formation of fresh crystal units. This, however, was just what must occur when a metal was annealed in such a way that the crystals grew in size and diminished in number. That process might be imagined as a gradual pushing forward of the amorphous layer between two crystals when one grew at the expense of the other in such a way that a small region of amorphous metal would receive a few molecules from one of the crystal units of the neighbouring crystal, thus constituting a new crystal unit of the growing crystal, while the robbed crystal unit of the other crystal would be broken up into a small amorphous mass. Such a process would gradually result in the coalescence of adjacent masses of amorphous cement owing to the gradual reduction of the total area of boundaries in the material, with the resulting formation of fresh crystal units from these coalesced amorphous particles. In that sense the amorphous cement would be unstable at high temperatures, but that would be incidental to the process of crystal growth during annealing.

The mechanical properties of metals and alloys at high temperatures had not been dealt with in detail in the present paper, and he (Dr. Rosenhain) would be very much interested in Dr. Bengough's foreshadowed further results. Meanwhile, however, he might say that concurrently with the experiments described in the present paper a great deal of work on the mechanical properties of metals at high temperatures had been carried out in his (Dr. Rosenhain's) laboratory and the results furnished some very definite support for the theory of the amorphous cement. Those mechanical and microscopic results on the effects of strain at high temperatures would, he hoped, be ready for publication shortly, but for the moment he could only state generally that the theory of an amorphous cement furnished simple explanations for a whole series of phenomena which would be difficult to understand on any other basis.

Professor Howe had raised an interesting point in his communication, and although a good many considerations could be urged against his suggestion that the line of fracture should follow near to, although not through or along the actual boundaries, it seemed probable to the authors

that if there is an amorphous layer between adjacent crystals the transition from the completely crystalline to the completely amorphous might not be entirely abrupt. A more or less gradual transition was suggested, for instance, by Dr. Beilby, when describing the surface structure of polished metal. But even apart from this, there must be a very strong adhesion between the amorphous cement and the adjacent layers of the crystal, and such adhesion would serve as a strengthening support tending to divert the line of fracture from the immediate vicinity of the boundaries. Further evidence on this point would, however, be forthcoming very shortly.

Finally, Dr. Rosenhain and Mr. Ewen had not expected that their hypothesis would be readily accepted, even with what they believed to be the strong experimental support which they had offered. Such a theory required the convergent support of many lines of independent evidence, and, in the course of time, they hoped that such evidence would be obtained. It must, however, be borne in mind that the very nature of the subject made experimental inquiry a difficult matter, and therefore all evidence must necessarily be indirect. The first step in the compilation of the requisite mass of evidence had, they hoped, been taken in the present paper, and with the aid of the criticism which they had sought by publication they hoped to approach the subject again at an early date.

THE SOLIDIFICATION OF METALS FROM THE LIQUID STATE.*

BY G. T. BEILBY, LL.D., F.R.S. (MEMBER OF COUNCIL).

THE problem which the Committee appointed by the Council, as a result of a suggestion thrown out in my May Lecture † (1911), proposes to investigate may be stated thus: *Does molecular aggregation occur in liquid metals immediately before solidification either by the formation of liquid crystalline units or by the segregation of globules enclosed in foam cells?*

Quincke has stated that a "foam-cell" structure in the liquid precedes solidification, and that this structure persists in the resulting solid. The liquid separates into two constituents, for even the purest substances contain sufficient impurity to produce an eutectic, and the primary constituent segregates in globules which are kept apart by "foam walls," which are composed of the eutectic or second constituent. As the segregation occurs in the liquid state the question which of the constituents will separate in globules will be settled by their surface tension. Thus an emulsion may consist mainly of globules encased by comparatively thin cell walls, or of a few globules separated in a large mass of liquid. ‡

The present author has shown (May Lecture, 1911) that gold globules solidified from the liquid state consist of sac-like grains, which retain their individuality even after very considerable deformation, when, for instance, the globule has been completely flattened by the blows of a hammer.

For convenient reference two of the figures from the Lecture are reproduced here. Fig. 1 is the flattened globule showing these sac-like grains, and Fig. 2 is the globule after it has been annealed at about 300° C. The structure of the undeformed globule was undoubtedly crystalline, each of the sac-like grains containing only similarly oriented units. On annealing, recrystallization takes place, and the new structure

* Read at Autumn General Meeting, London, September 25, 1912.

† *Journal of the Institute of Metals*, No. 2, 1911, vol. vi. p. 16.

‡ *Proceedings of the Royal Society*, vol. lxxvi. A., 431.



FIG. 1.
Gold globule with "primary
grains" distorted by
hammering.



FIG. 2.
Gold globule with "secondary
grains" developed by anneal-
ing at 300° after hammering.

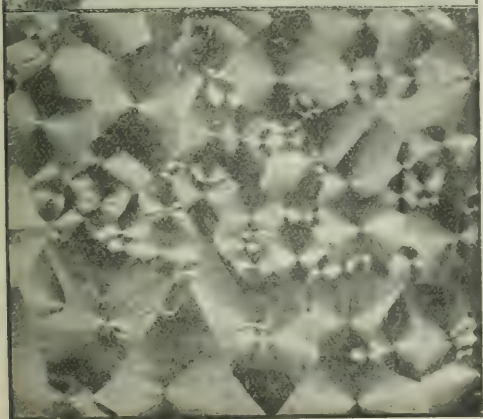


FIG. 3.
Cell-like structure developed
by crystalline growth from
nuclei in a thin film on glass.

which results is sharply crystalline and quite different from the sac-like type of the primary grains. These observations led the author to ask whether this sac-like structure is to be regarded as due to the persistence of a structure which originated, as Quincke suggests, while the metal was still in the liquid state, or whether it is to be regarded as a direct result of crystallization during solidification. Although the distinction between the two types of crystallization has been referred to more than once, it may be permissible to enlarge on the matter here. Probably many metallographers are familiar with the sac-like type of grains which are occasionally produced under particular conditions of cooling, but the essential difference between this type of crystallization and that which occurs on the recrystallization of a mass of metal which has previously been strained, either by cold working or by local cooling and shrinkage in an ingot or other casting, does not seem to have been so generally recognized. It is therefore now suggested that the terms "primary" and "secondary" should be used in describing these two distinct types, at any rate in all cases where it is desirable to distinguish between them. It is clear that in any inquiry as to the existence and origin of sac-like grains the distinction between these two types must be kept fully in mind. Foam-cell formation, if it occurs, will mainly affect grains of the "primary" type. Crystals of the "secondary" type are probably formed not by the transport of molecules within the mass, but by orientation of molecules *in situ*.

In experimental investigations connected with the present inquiry it will be necessary to produce unstrained crystals of the "primary" type. For this purpose any form of chill or ingot mould would be unsuitable, as cooling and contraction strains can hardly be avoided in these forms of casting. The author has experimented mainly with globules formed by fusion in the blowpipe flame. Probably the method so successfully used by Ewing and Rosenhain* of pouring liquid metal on a flat horizontal surface would in most cases ensure that the crystallization of the mass is of the unstrained primary type.

* *Philosophical Transactions*, vol. cxciii. A., 1900.

If it be granted that the "primary" crystals are enclosed in cells of some sort, the present inquiry will then take the following form:—Are these cells formed at the final stage of crystallization or are they formed while the metal is still liquid, and further, if the cell formation is pre-arranged in the liquid state, are the initial steps due to liquid segregation and surface tension, or to the crystalline aggregation of molecules in the liquid state?

When the process of crystallization is watched under the microscope as it takes place in a thin layer of liquid on glass or other flat support, it appears to start from isolated nuclei, solidification and crystal growth proceeding radially from each nucleus till the radii from adjoining nuclei *almost meet*. It appears under fairly high magnification as if radii approaching each other stop short before they have actually met, and as if there is formed between them a slight ridge of neutral territory (see the forthcoming paper of Dr. Rosenhain and Mr. Ewen on "Intercrystalline Cohesion in Metals"). The effect when all the radii have thus been arrested is as if a network had been spread over the surface, the radii from each nucleus being enclosed by cell-like boundaries. This gives us a picture in *two* dimensions of what would occur if the layer of liquid was sufficiently deep to permit of similar growth in the third dimension, and we are thus provided with an illustration of a cell structure which is the direct outcome of crystal growth. Though this illustration may not hold in all its details for other types of crystallization, yet something at least analogous to the above must happen. The photograph, Fig. 3, is not magnified, but is if anything reduced from natural size. It is not to be expected therefore that the microscopic inter-crystalline boundaries should be visible. The figure, however, shows fairly well the features of this type of structure, and in particular it is seen that it is the nuclei which produce the grains. The growth began at the larger and more powerful nuclei, the small grains which are scattered over the surface of the larger grains only started to grow after the latter were well under way. If a growth of this kind be watched from beginning to end no doubt can be left in the mind of the observer *that in this case it is the nuclei which entirely control the*

ultimate structure. The cell-like structure which has been developed shows no trace of any pre-existing foam-cell structure derived from the liquid film, nor does it appear necessary to postulate the existence of this type of structure. It does not, however, appear to the author that illustrations of this kind are sufficient in themselves entirely to negative the foam-cell hypothesis; they only emphasize the necessity for more positive evidence if the hypothesis is to stand. If the hypothesis is well founded it ought to be possible to find cases in which the crystalline method of cell formation is controlled, or partially controlled, by the pre-existing structure. Among alloys or slightly impure metals it ought to be possible to find cases in which the pre-existing structure is so robust that it is able to resist or restrain crystalline growth; foam walls which by their superior rigidity are able effectively to partition up the whole space before cell formation from the crystalline nuclei can take effect. In the microstructure of certain alloys and impure metals surface tension forms, globular, dumb-bell, or rod-like, are often very pronounced; it is possible that the occurrence of these forms may supply a clue which it will be worth while to follow up.

It is not intended that the scope of the present inquiry should be restricted to the proof or disproof of the foam-cell hypothesis. The Council in its remit has indicated a wider range than this, and it is hoped that investigation will be encouraged, not only in the more theoretical regions covered by the work of Lehman, Tammann, Miers, and others on the earliest steps in crystallisation both in the liquid and solid states, but also on the more practical aspects suggested by observations on the influence (*a*) of temperature and (*b*) of mechanical agitation on the molten metal in determining the size and type of the grains which are subsequently found in the solidified metal.

In a substance like water, which expands on solidification, there are good grounds for the belief that the range from the maximum density at 4° C. down to the freezing point at 0° C. covers a period during which active molecular aggregation is occurring. Observations on bismuth and its alloys may show that a similar state of things is to be found in metals, and in

any case it is much to be desired that we should have refined and accurate density determinations of liquid metals in the neighbourhood of the solidifying point. The fact that the majority of metals contract on solidification, and therefore do not show the phenomenon of a point of maximum density some degrees above the solidifying point, need not blind us to the importance of these density determinations. It is probable also that the measurement of changes of electrical conductivity with temperature in the *liquid metals* would be a valuable aid in this inquiry.

In conclusion, it appears to the author that while it may not be possible to establish Quincke's view that in all cases solidification is preceded by segregation and the development of a "foam-cell" structure, yet that among recorded observations there are some which give colour to the view that at any rate in alloys and impure metals there is segregation under the influence of surface tension in the liquid or the partially solidified state.

The more general inquiry as to the changes which precede solidification in metals appears to be a promising territory which is awaiting exploration, and it is to be hoped that the preliminary inquiry which is about to be made into the work which has been done in the various pioneer camps which have approached this territory from various sides will lead to the establishment of new camps within the territory itself.

THE INFLUENCE OF IMPURITIES IN "TOUGH-PITCH" COPPER.*

WITH CHIEF REFERENCE TO ANTIMONY.

BY FREDERICK JOHNSON, M.Sc., A.I.M.M.

(HEAD OF METALLURGICAL DEPARTMENT, SWANSEA TECHNICAL COLLEGE).

INTRODUCTION.

IN continuation of a series of experiments carried out with a view to ascertaining and placing on record the varied influences of traces of impurities on the useful properties of copper, the author now presents the results of experiments which, in the main, have been directed toward the determination of the influence of antimony on "tough-pitch" copper.

More than any other property, it is desirable that commercial copper should possess the property of malleability at a red-heat.

Copper which is "red-short" is the *bête noire* of the manufacturer, and experiments which indicate the nature and extent of the influence of impurities on this property cannot fail to be of service to him.

Assuming that copper containing impurities can be successfully rolled hot, it remains to show whether such copper will have mechanical properties inferior, equal, or superior to those of pure copper, and to show also, if possible, the structural condition of those impurities.

PREVIOUS INVESTIGATIONS.

Of previous investigations, that of Hampe † demands first attention. He found that:—(1) Copper with 0.529 per cent. antimony could be drawn into wire. (2) Copper with 1 per cent. antimony was extremely "red-short." (3) Antimony

* Read at Autumn General Meeting, London, September 26, 1912.

† *Chemiker Zeitung*, 1892, No. 42.

in small amounts increased the tenacity of copper, but lowered its conductivity.

Dealing with its presence in copper in the form of salts, Hampe discovered several notable facts in addition to the foregoing.

As antimonate of copper, no "red-shortness" was experienced when there was sufficient present to correspond to 0.5 per cent. antimony, whereas with 0.5 per cent. antimony in the metallic form incipient "red-shortness" was produced.

A point which Hampe appears to have overlooked, however, is that when a compound such as the foregoing is added to a molten metal which dissolves it, it does not necessarily follow that that compound will retain its individuality in the solidified metal, although its effects may be less harmful than those of metallic antimony. As will be shown later, when antimonious oxide (Sb_2O_3) is added to molten copper, it is decomposed by the copper, and does not exist as the original, unaltered compound after the metal has solidified and cooled.

Experimenting with antimonate of bismuth, Hampe stated that neither red-shortness nor cold-shortness occurred with less than 0.7 per cent. of this compound. That the protective influence of antimony and oxygen in the presence of so much bismuth can be so marked is open to grave doubt.

Hiorns* and Lamb place the limit of antimony as 0.6 per cent. for wire-drawing. With more than this amount, wires could not be successfully produced. They also found that antimony very seriously lowered the electrical conductivity (0.10 per cent. causing a lowering of 24 per cent.), increased the hardness, had a decolorising effect, and was less efficient than arsenic in producing soundness.

Hiorns,† as a result of experiments on the cold rolling of small ingots, concluded that:—(1) Arsenic and antimony were better than antimony alone. (2) Antimony (0.20 per cent.) when added to copper containing lead (0.2 per cent.) diminished the brittleness caused by the lead.

With regard to the joint action of antimony and oxygen

* *Journal of the Society of Chemical Industry*, May 15, 1909.

† *Ibid.*, July 1906.

he assumed that antimony would react with cuprous oxide to form the higher oxide, Sb_2O_5 .

Greaves* investigated the influence of oxygen on copper in the presence of antimony, and found that an increase of oxygen had no definite effect on the tensile strength of cast copper containing a constant percentage of antimony, but caused a serious reduction in ductility, as measured by percentage elongation. As will be shown later, this is not true for rolled, annealed rods.

Greaves also found that where the electrical conductivity had been lowered by antimony, the addition of oxygen tended, to a slight extent, to neutralize that effect, causing a slight recovery of conductivity.

T. Johnson† gave the following results of tests on antimonial copper:—

	Tensile Strength. Tons per Sq. Inch.	Elongation per Cent. on 2 Inches.
Copper with 0.25 per cent. antimony .	15.17	49
„ 0.50 „ „ .	15.60	45

The oxygen contents were not given, but some oxygen was undoubtedly present.‡ The ingots were rolled hot and cold, and the strip annealed before testing.

Lewis§ concluded, from a series of rolling experiments on copper containing added quantities of impurities, that arsenic had the property of neutralizing the injurious effect of antimony, 0.10 per cent. antimony having a worse effect on the hot-working properties than the same amount in the presence of 0.6 per cent. arsenic.

Archbutt|| confirmed the harmlessness of antimony on the hot-working properties of copper.

It will be seen that, of all the foregoing investigators, one only (T. Johnson) produced ingots strictly comparable with those of commerce—that is to say, in the “tough-pitch” condition.

The author observed the last-named condition by carrying

* *Journal of the Institute of Metals*, No. 1, 1912, vol. vii. p. 218.

† *Birmingham Metallurgical Society Proceedings*, March 8, 1906.

‡ Private communication.

§ *Engineering*, December 4, 1903.

|| *Journal of the Institute of Metals*, No. 1, 1912, vol. vii. p. 263.

out his experiments in a similar manner to that previously adopted.* The purest electrolytic copper (procured from Messrs. Vivian & Sons, Swansea) and chemically pure antimony were used.

Influence of Antimony during the Poling Operation.—By noting the behaviour of small trial-ingots, the author was able to record a number of interesting facts. (1) That with antimony present up to 0·3 per cent., the copper has splendid hot-working properties, either under or up to “pitch.” (2) That with more than 0·3 per cent. antimony, the removal of oxygen by poling is synchronous with inferior hot-working properties. This observation is borne out by the behaviour of ingots A1 and AA1 (see Table I. and also Fig. 1). The poling in the case of A1 was pushed beyond the “tough-pitch” stage (in so far as the percentage of oxygen is concerned). This is explained by the following observation:—(3) That, although the influence of antimony is to render the copper “red-short” (after the removal of oxygen), and thus “overpoled” according to one interpretation of the term, yet its effect is really to prevent “overpoling” as indicated by the “rising” or “spewing” of an ingot. The two latter terms are used to describe the physical phenomena exhibited by an overpoled ingot during solidification. The raising of the surface or the ejection of molten copper through the top crust of the ingot are due to the escape of gases which excessive poling has introduced into the copper.

Either the action of these gases is neutralized, or their entry into the molten copper opposed, by the antimony. The author prefers the latter explanation.

It is, therefore, possible to cast an ingot (A1) which, owing to the presence of antimony, has a level surface, but which, were it free from antimony, would “rise” or “spew” after so much “poling.” The removal of the oxygen has, however, from the rolling point of view, caused the ingot to be “red-short” (see Fig. 1). On the other hand, the “underpoled” ingot (AA1), as will be seen from the photograph, has rolled splendidly, but this property has been gained at too great a cost, because the oxygen in excess seriously affects the

* *Journal of the Institute of Metals*, No. 2, 1910, vol. iv. p. 174.

toughness and cold-working properties of the copper, and also causes a depression to form on the surface of the ingot. This depression is closed up during the rolling, and remains in the rod as an unseen but dangerous flaw.

All the ingots used in this research, with the exception of AA1, had level surfaces.

Referring again to the influence of antimony in checking the absorption of gases during poling, it may be pointed out



FIG. 1.

AA1 contains antimony	0.5 per cent. ;	oxygen	0.33 per cent.
A1 " "	0.5 " ;	" "	0.02 "
L2 " lead	0.35 " ;	" "	0.012 "

that it is not without its value nor its danger in the refining of "tough" copper. There is nothing so trying in the refinery as a charge which has gone "over the pitch." "Spewing" ingots (cakes, billets, &c.), inferior malleability, lost time in bringing the charge back to "pitch," all contribute to give the refiner much anxiety. Any impurity in the copper which will check this tendency of the charge (under certain conditions) to go "over the pitch" is, therefore, welcome.

Arsenic is such an impurity, and the author has just shown that antimony is another. A little antimony even in arsenical copper should also be beneficial. Lead has always been recognized as having a similar influence, but lead is wholly undesirable in wrought copper.

Having pointed out the value of a little antimony, it now remains to indicate the danger. This lies, of course, in having too much present, and so masking the true "pitch" of the copper, that it is "red-short" before the other signs of "overpoling" or going "over the pitch" have become apparent.

There is yet another side to the question. Antimony hardens copper for rolling, and this becomes serious if it prolongs the "breaking-down" operations. For a normal, soft, tough arsenical copper, however, the author considers that 0.10 per cent. antimony would be a beneficial addition. The presence of other impurities would modify this proportion.

Such copper could not be used for making malleable alloys, e.g. brass.

From high conductivity copper, also, antimony must be rigidly excluded.

Incidentally the author would like to dispose, once and for all time, of the fallacy that pure electrolytic copper is immune from "overpoling." The statement has been made by well-known metallurgists so often that it demands immediate refutation. Such copper has, possibly, a greater solvent power for gases than most less pure brands, and, in addition to meeting with overpoled electrolytic copper in the refinery, it has been the author's experience that "tough-pitch" ingots of electrolytic copper are the most difficult of all to produce on an experimental scale. Such copper, although never becoming "red-short," is just as liable to become porous or to "spew" after overpoling as any other kind, and more liable than many kinds.

THE ROLLING OF INGOTS.

The ingots ($1\frac{1}{4}$ inch square) were rolled at a red-heat about 900° C. (the usual temperature for rolling arsenical copper, as

judged by an experienced hand) in the works of Messrs. Vivian and Sons at Margam (Port Talbot). They were rolled hot in six passes to $\frac{11}{16}$ inch diameter, finishing at a dull red-heat, annealed by raising to a bright red-heat, quenched in the pickling bosh (to remove scale), and then rolled cold to $\frac{5}{8}$ inch (full). Finally, they were drawn once through a die to straighten and to confer on them a smooth and truly round surface. These rods will subsequently be designated "as rolled."

Their compositions are given in Table I.

TABLE I.

Mark on Rod.	Antimony per Cent.	Arsenic per Cent.	Oxygen per Cent.	Appearance of Ingot.	Behaviour during Rolling.
RR	nil	nil	0.050	Level surface.	Rolled perfectly.
A3	0.2	nil	0.058	Do.	Do.
A2	0.29	nil	0.054	Do.	Do.
AA2	0.3	nil	0.063	Do.	Do.
A1	0.5	nil	0.02	Do.	Red-Short at 3rd pass. (See Fig. 1.)
AA1*	0.49	nil	0.33	Surface depression.	Rolled perfectly.
A	0.2	0.36	0.065	Level surface.	Do.

* Rod AA1 was prepared purposely with a considerable excess of oxygen.

BEHAVIOUR OF THE INGOTS DURING ROLLING.

All the ingots offered more resistance in their passage through the rolls even at a red-heat than the pure copper ingot, RR, which had a rougher surface, owing to its greater softness and its inability to resist the "scoring" action of the rolls.

Ingot A1 was red-short, and was removed from the rolls at the third pass.

METHODS OF ANALYSIS.

Oxygen.—The method was similar to that described in a former paper by the author.* In order, however, that the fears of the ultra-exact might be allayed, the author prepared the strips for analysis by cold rolling. Thus there was no

* *Journal of the Institute of Metals*, No. 2, 1910, vol. iv. p. 185.

formation of scale, necessitating the instantaneous treatment in dilute acid for its removal. This superficial "pickling," which aroused criticism, has been proved by the author to be perfectly harmless. However, the removal of scale by means of emery-paper is more effective, and is necessary, in any case, even after pickling.

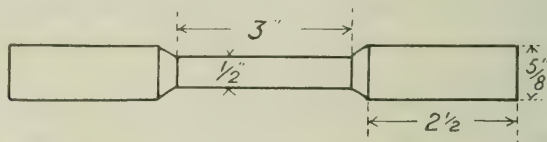
In the train of wash-bulbs, one containing silver nitrate was substituted for the one containing mercuric chloride. Any arsenuretted or antimoniuiretted hydrogen from the hydrogen generator is thus arrested.

Antimony.—This was determined by several methods, but the method finally adopted for all the rods was that in which pure ferrous sulphate is added after oxidation to a nitric acid solution of 10 grammes of copper (more if only traces of antimony). Ammonia is added in excess; the ferric hydrate carrying down the antimony as basic antimonate of iron. Arsenic is also similarly carried down if present. The precipitate is redissolved in hydrochloric acid, gassed with sulphuretted hydrogen, the mixture of sulphides (in most cases only copper and antimony sulphides) treated with 10 per cent. potassium sulphide to extract the antimony sulphide (Sb_2S_3). The Sb_2S_3 is reprecipitated by acidifying with dilute sulphuric acid, then dissolved in strong hydrochloric acid after boiling and filtering (any arsenic sulphide (As_2S_3) being left behind on filter). Bromine is added, reduction effected by sodium sulphite, and the antimony titrated with potassium bromate.* The author has tried the methods of distillation which depend upon raising the boiling points of the solvent used in order to reach the distillation temperature of antimonious chloride. The methods suffer from the disadvantages of demanding constant attention, and of being expensive in distilling-flasks, unless flasks of fused silica ware are used. The author invites discussion on the merits of distillation methods for antimony in copper. Arsenic was determined by distillation as usual.

* Duncan, *Chemical News*, February 7, 1901.

PREPARATION of TEST-PIECES.

(1) *Tensile Test-Pieces*.—Portions of the rods were sawn off, and turned down to $\frac{1}{2}$ inch for a gauge-length of 3 inches full, the 3-inch length being marked off exactly. The finished test-piece had dimensions as given in the accompanying sketch.



(2) *Alternating Stress Test-Pieces*.—These were for Dr. Arnold's testing-machine, and 6-inch lengths of rod were turned down to $\frac{3}{8}$ inch diameter.

(3) *Compression Test-Pieces*.—Small cylinders were prepared from the rods ($\frac{5}{8}$ inch diameter by 1 inch) by facing down in the lathe.

ANNEALING.

The test-pieces were annealed at 800° C. for 15 minutes.

The reheating-annealing of the cast ingots is particularly beneficial in the case of antimonial copper, as the solid solution in the cast state is greatly lacking in uniformity. A thorough reheating assists diffusion and produces greater uniformity.

THE MECHANICAL TESTS.

On reference to Table II., the outstanding facts are as follows:—(1) Antimony raises the tensile strength of "tough-pitch" copper, and slightly lowers the percentage elongation. (2) The annealed rods give results better for purposes of comparison than cold-worked rods before annealing. (3) Where cuprous oxide is in large excess, cold work has a seriously embrittling effect. Rod AA1 has an astonishing percentage recovery of ductility after annealing (over 600 per cent. as compared with less than 300 per cent. in the case of the "tough-pitch" rods). (4) Antimony (0.2 per cent.) has no ill effect on arsenical "tough-pitch" copper.

Mark on Rod.	Rods as Rolled.		Rods Annealed.		Composition.		
	Tensile Strength. Tons per Sq. In.	Elongation per Cent. on 3 Inches.	Tensile Strength. Tons per Sq. In.	Elongation per Cent. on 3 Inches.	Oxygen per Cent.	Arsenic per Cent.	Antimony per Cent.
RR	19.80	14.7	14.33	51.3	0.05
A3	19.50	13.0	14.25	43.3	0.058	...	0.2
A2	19.44	16.7	14.95	46.0	0.054	...	0.29
AA2	19.55	13.0	14.64	48.3	0.063	...	0.3
AA1	20.30	6.0	15.16	44.7	0.33	...	0.49
A	20.16	15.3	14.92	48.7	0.065	0.36	0.2
TABLE IIA.							
L1	18.33	17.3	14.7	53.3	0.023	0.39	Tin per Cent. Lead per Cent.
T	19.84	14.0	15.48	41.7	0.05	0.37	0.18 ...

TABLE III.—*Dr. Arnold's Alternating Stress Tests.*

Mark on Rod.	No. of Alternations.		Percentage Increase in Toughness due to Annealing.	Composition.			Remarks.
	As Rolled.	Annealed.		Oxygen per Cent.	Arsenic per Cent.	Antimony per Cent.	
RR	118	244	107	0.05	Fracture-line central; silky.
A3	136	210	54	0.058	...	0.2	" " eccentric; silky.
A2	116	268	131	0.054	...	0.29	" " central; silky.
AA2	118	258	110	0.063	...	0.3	" " " "
AA1	49	138	181	0.33	...	0.49	Very broad serrated fracture-line; dry
A	119	258	116	0.065	0.36	0.2	Fracture-line central; silky.
TABLE IIIA.							
L1	169	238	41 *	0.023	0.39	Tin p. Cent. Lead p. Cent.	Fracture-line central; silky.
T	134	265	98	0.05	0.37	0.19	" " " "

* The abnormal toughness of bar L1 in the cold-worked state as compared with the others is due to the low percentage of oxygen, thus affording further proof of the embrittling influence of cuprous oxide during cold work.

In Table III. the results of the alternating-stress tests are recorded, and the chief points of interest are as follows:— (1) Antimony up to 0.30 per cent. does not decrease the toughness of "tough-pitch" copper, nor does 0.2 per cent. antimony decrease the toughness of arsenical "tough-pitch" copper. (2) Cuprous oxide in excess very seriously lowers the toughness, more so in the rolled than in the annealed rod. (3) Rod A3 shows abnormal behaviour. It will be shown later that this is due to lack of uniformity.

The compression test-pieces were crushed down under a steam-hammer from cylinders 1 inch long by $\frac{5}{8}$ inch diameter to discs $\frac{5}{16}$ inch by $1\frac{1}{4}$ inch diameter.

These tests showed that, in the case of the annealed specimens, the quality of the copper in no degree suffers deterioration on account of the presence of antimony. With regard to the unannealed specimens, these all showed signs of the strains previously caused by the cold rolling. They all developed minute incipient cracks round the bulging circumference of the disc, these being most marked in the case of specimen AA1 (rich in cuprous oxide). The excessive embrittling influence of the cuprous oxide was removed by annealing, thus confirming the tensile and alternating-stress tests. The annealed specimen showed no cracking indicative of brittle metal, but one large fissure was developed, corresponding to the inevitable flaw in the rod, due to the original surface depression of the underpoled ingot. This depression had been closed up in the rolling process, causing a hidden longitudinal flaw, which naturally yawned open as the test-piece was spread out by the blows from the hammer.

COLD-ROLLING TESTS.

Short pieces of the $\frac{5}{8}$ inch rods as rolled were sawn off, annealed (20 minutes at 900° C.), and quenched.

These were rolled cold into flat strips $\frac{1}{8}$ inch thick without further annealing.

Test-pieces RR, A, A2, and AA2 (Fig. 2) showed no edge-cracking whatever.

Incipient edge-cracking occurred in the case of A3.

AA1 was again the worst of all, edge-cracking starting when a thickness of $\frac{3}{16}$ inch had been reached.

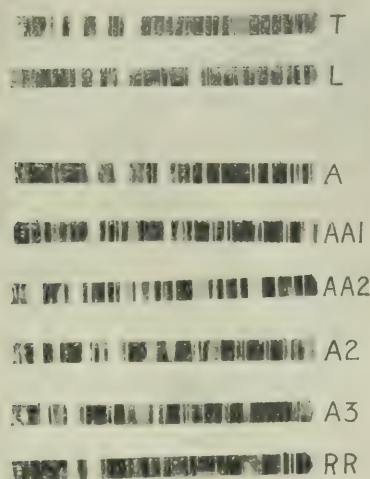


FIG. 2.

MICROSTRUCTURE.

All the rods as rolled showed a uniform, crystalline structure with frequent "twinning." With regard to "oxidules," the appearance of the rods under the microscope differed from one another. They are given in Table IV.

The segregation of the cuprous oxide quite explains the abnormal behaviour of rod A3 in the mechanical tests (see Tables II. and III.), also the eccentricity of the final fracture line in the alternating-stress tests. Normal rods show a fracture line across the centre of the test-piece (see *a* of accompanying sketch). Rods which are not uniform yield more to the stresses on their weaker side, and the final fracture line occurs nearer to the stronger side (see *b*).



On referring back to the rough notes made when preparing the ingots, the following entry was found:—

"Ingot A3 perfectly level, but poured rather cold."

Here, then, possibly lies the explanation of the lack of uniformity in the ingot. A portion of the molten metal (probably the last to enter the mould) was richer in oxide than the remainder, and, on account of the metal being cold, solidification proceeded so rapidly that this oxide had no chance to diffuse uniformly throughout the ingot and was trapped *in situ*.

TABLE IV.

Mark.	Antimony per Cent.	Oxygen per Cent.	Appearance under Microscope.
RR	nil	0.05	Light-blue oxidules (cuprous oxide) uniformly distributed.
A3	0.2	0.058	Dark, slate-coloured "oxidules." Some segregated cuprous oxide (see Fig. 2).
A2	0.29	0.054	Dark oxidules. No cuprous oxide. Uniform.
AA2	0.3	0.063	Do. Also cuprous oxide. Do. *
AA1	0.49	0.33	Considerable excess of cuprous oxide, accompanied by a few dark "oxidules." In the cast ingot, more than half the field is occupied by copper-cuprous oxide eutectic. During rolling this was broken up and the microstructure shows the parallel trains of "oxidules" (cuprous oxide) in lines following direction of rolling (see Fig. 3).
A	0.2	0.065	Dark oxidules. A little free cuprous oxide.

Fig. 1, Plate XXVII., shows the complete absence of cuprous oxide from one area of the specimen, whilst Fig. 2, Plate XXVII., is typical of the oxide-rich area. In order to obtain better contrast for photographing, the specimen was heat-tinted for this photomicrograph. The cuprous oxide showed up as pale-green spots on a blood-red field (white spots on a black background in Fig. 2, Plate XXVII.). Before heat-tinting, the "oxidules" appeared pale-blue on pink background of copper, a combination difficult to reproduce effectively by photography.

* Nearly all the "oxidules" in AA2 resemble that shown in Fig. 7, Plate XXVIII. There are one or two isolated "oxidules" similar to that shown in Fig. 8, Plate XXVIII.

THE STRUCTURAL CONDITION OF ANTIMONY IN
"TOUGH-PITCH" COPPER.

A number of experiments were made by adding to copper (from which all oxygen had been carefully excluded) metallic antimony alone, antimonious oxide (Sb_2O_3) alone, and metallic antimony *plus* cupric oxide.

The details are given in Table V.

TABLE V.

No.	Antimony per Cent.	Oxygen per Cent.	Nature of Impurity added.
I.	0.5	nil	Metallic antimony.
II.	0.5	0.12	Metallic antimony and cupric oxide.
III.	0.5	0.25	" " " "
IV.	0.1	0.12	" " " "
V.	0.5	0.10	Antimonious oxide.
VI.	0.5	0.10	" " " "
VII.	4.03	0.97	" " " "

In alloy I., most of the antimony was in solid solution, and etching revealed the usual "core" structure, in the light antimony-rich fringes of which a very little free Cu_3Sb was visible. This constituent, the composition of which is given by Hiorns, is very pale-blue in colour (paler than cuprous oxide), and is best seen before etching.

In alloy II., the oxygen appeared not as cuprous oxide, but as dark slate-coloured "oxidules." Caustic soda or potash should not be used to remove grease from the surface of the specimen, as it attacks the antimonial "oxidule," leaving only a pit which appears black under the microscope. These antimonial "oxidules" are shown in Fig. 4, Plate XXVII., and occur in all the other alloys, whether cuprous oxide is in excess or not.

Wherever oxygen occurs in excess of that demanded by that part of the antimony which is not in solid solution, it exists as pale-blue cuprous oxide, which forms a ternary eutectic with the solid solution and the antimonial "oxidules."

Fig. 5, Plate XXVIII., shows the solid solution of antimony

in copper (dark-etching "cores" with light antimony-rich fringes) surrounded by eutectic.

The constituents of the eutectic under higher powers show peculiar behaviour in their relative disposition. Either the slate-coloured antimonial constituent or the light-blue cuprous oxide forms here and there as a crescent or circle enclosing a globule of the other constituent.

In Fig. 6, Plate XXVIII., are seen two of these circlelets of cuprous oxide, the centre one enclosing both copper (light half) and the antimonial constituent (dark half). In the lower portion of the micrograph, a dark antimonial "oxidule" is seen, and several smaller ones are dotted here and there in the upper portion of the field.

Fig. 7, Plate XXVIII., illustrates an area of the same specimen showing another composite "oxidule," the antimonial portion forming the enclosing crescent in this case, the cuprous oxide globule being enclosed.

As to the true composition of the antimonial constituent, the author can make no definite statement. In fact, its composition seems variable; in some cases having a definitely duplex structure as shown in Fig. 8, Plate XXVIII. This shows a slate-coloured "oxidule" containing numerous particles of a blue colour (probably cuprous oxide). In other cases the "oxidules" contain coppery streaks which may possibly be the metallic reduction product of a reaction between a reducing-gas such as carbon monoxide on cuprous oxide. These coppery streaks are sometimes seen in the centre of cuprous oxide "oxidules" in ordinary commercial copper, and there may be some connection between them and the gases present.

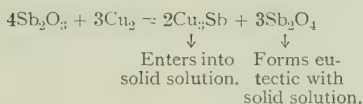
Possibly the checking influence of antimony on "spewing" may find an explanation in the absorptive power of its "oxidules" for gases, but the author is unable to support this explanation.

It seems to be clear that the antimony exists in the higher state of oxidation (Sb_2O_4), because in alloy VII. (Table V.), although the antimony was added in the form of antimony trioxide (Sb_2O_3), it split up into antimony—which formed Cu_3Sb , and partly entered into solid solution—and the slate-

coloured constituent already described. Whether the latter is Sb_2O_4 alone, or a compound of Sb_2O_4 with Cu_2O (antimonate), whether it is capable of merely dissolving copper or Cu_2O , or whether, if this be true, it deposits the dissolved substance when cooling, further research may show.

An examination of alloy VII. under the microscope showed no Cu_2O , but such an amount of free Cu_3Sb in addition to that which was in solid solution as would represent, roughly, about one-third of the antimony present.

The author suggests the following reaction:—



For antimonial copper, it would seem that the less antimony which is allowed to enter into solid solution (*i.e.* the more which exists as “oxidules”) the higher will be the electrical conductivity (see p. 194).

When oxygen is present, as much free Cu_3Sb is converted into “oxidules” as the oxygen will account for. In the case of bar A1 (see Table II. and Fig. 1), so much oxygen had been removed by poling that, in all probability, some free Cu_3Sb separated out.

In order to show whether, by increasing the oxygen in order that all the antimony not in solid solution would exist as harmless “oxidules,” the author made the following experiments:—

TABLE VI.

Mark on Ingot.	Antimony per Cent.	Oxygen per Cent.	Remarks.
A5	0.5	Undetermined	Under pitch. Forged perfectly.
A5	0.5	0.13	Up to pitch. „ „ Bent double cold.
A6	1.0	Undetermined	Under pitch. „ „
A6	1.0	0.25	Up to pitch. Forged fairly well. Incipient cracking. Bent double cold.
A7	1.0	nil	Decidedly red-short. Free Cu_3Sb discernible under the microscope.

Small ingots were cast, particulars of which are given in Table VI. Ingots A5 and A6 were forged at a red-heat

when "under pitch," then remelted, and brought up to pitch. All three ingots were reheated side by side, and forged at a red-heat. The results are given in Table VI., and show that it is possible to forge copper hot, even with 1 per cent. antimony, if sufficient oxygen be present to prevent the occurrence of free Cu_3Sb .

EXPERIMENTS WITH TIN AND LEAD.

These experiments, whilst far from being sufficient, are of such interest, and the possibility of their continuance so uncertain at present, that the author has decided to place them on record.

The ingots were prepared in exactly the same way as the antimonial ingots, and were rolled and tested at the same time and under exactly similar conditions.

INFLUENCE OF LEAD ON "POLING" OPERATION.

From the behaviour of trial ingots the author proved that:—

1. Lead (in the proportions used) caused "tough-pitch" arsenical copper ingots to "sink" in the moulds. That is to say, an ingot which would otherwise have had a level surface had a longitudinal surface depression after the addition of lead.

2. By "poling" the metal in order to produce an ingot with a level surface, so much oxygen was removed that in one case (ingot L2) the ingot was so "red-short" as to be shattered during the first pass through the rolls at a red-heat (see Fig. 1). There were also strong indications that with the smaller percentage of lead (0.18 per cent.) it would be possible to carry "poling" so far (without the ingot spewing) as to produce "red-shortness."

In fact, ingot L1 was produced by remelting the rolled strip of a previously prepared ingot, which had shown edge-cracking at a red-heat. The oxygen, unfortunately, was not determined in this strip before remelting, but it was probably lower than in L1. In Table VII. the analyses of the ingots and a record of their behaviour appear.



FIG. 1.—Showing absence of "oxidules" in one part of rod A3.
Magnified 200 diameters. V. unetched.



FIG. 2.—Showing segregated "oxidules" (pale-green spots on blood-red ground). Rod A3.
Magnified 500 diameters. V. heat-tinted.



FIG. 3.—Showing excess of cuprous oxide in rod AAl.
Antimony, 0.50 per cent. ; oxygen, 0.33 per cent.
Magnified 150 diameters. V. unetched.

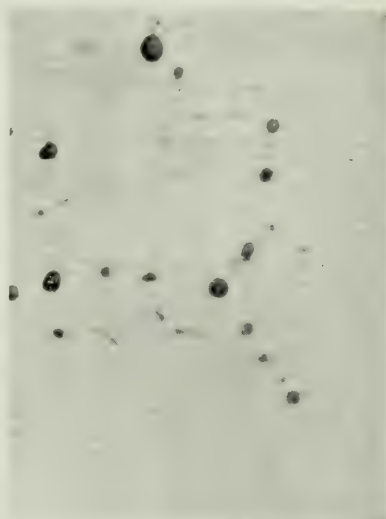


FIG. 4.—Alloy II., Table V. Shows dark slate-coloured antimonial "oxidules."
Antimony, 0.5 per cent. ; oxygen, 0.12 per cent.
Magnified 400 diameters. V. unetched.

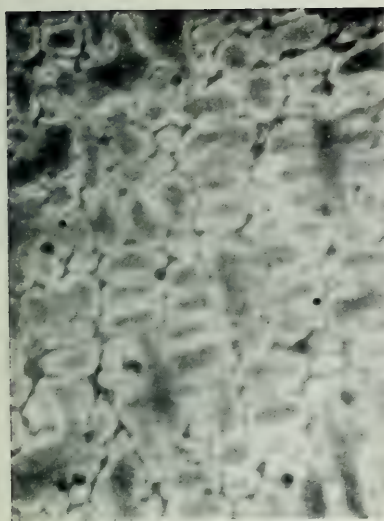


FIG. 5.—Alloy VI., Table V.
Antimony, 0.50 per cent. ; oxygen, 0.10 per cent.
Magnified 70 diameters. V. etched.

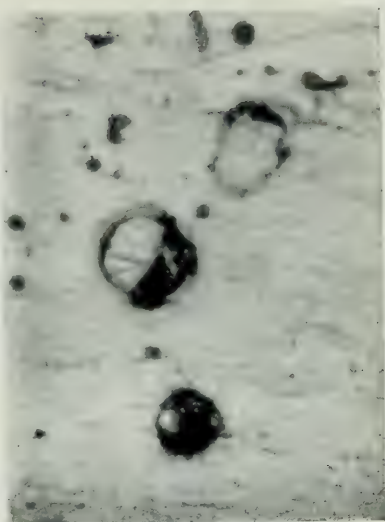


FIG. 6.—Same alloy as Fig. 5.
Magnified 900 diameters. V. unetched.

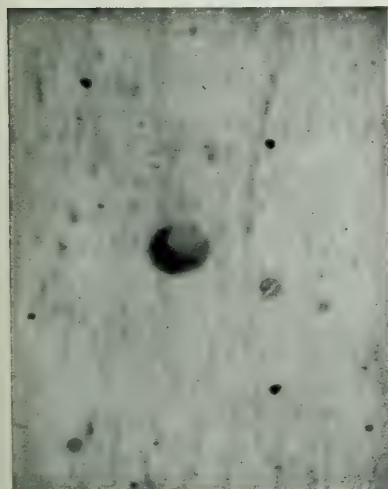


FIG. 7.—Same alloy as Fig. 5.
Magnified 900 diameters. V. unetched.

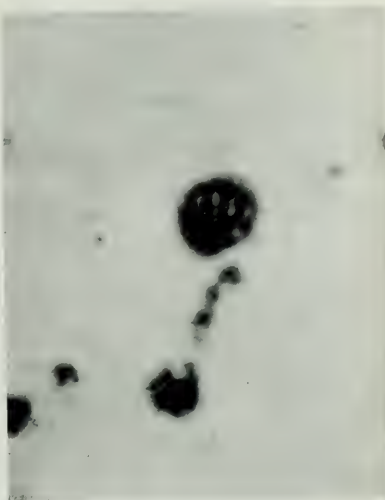


FIG. 8.—Same alloy as Fig. 5.
Magnified 900 diameters. Unetched.

INFLUENCE OF TIN.

The influence of tin seems to be to harden arsenical copper for hot and cold working, and to raise the tensile strength more than any other of the elements tried. The record of the mechanical tests appears in Tables IIA and IIIA. Apart from causing a peculiar, irregular bulging at the circumference of the hammered annealed discs, the specimens containing tin and lead showed no difference of behaviour from the other specimens in the crushing-down tests.

TABLE VII.

Mark on Ingot.	Oxygen per Cent.	Arsenic per Cent.	Lead per Cent.	Tin per Cent.	Appearance of Ingot.	Behaviour in Rolling.
L1	0.023	0.39	0.18	nil	Dead level.	Very good.
L2	0.012	0.38	0.35	nil	„	Smashed at first pass.
T	0.05	0.37	nil	0.19	Very slight depression. A few pin-holes near surface.	Very good. Forged hard. Good smooth surface.

CONCLUSIONS.

1. Antimony up to 0.5 per cent. has no detrimental influence on the hot-forging qualities of "tough-pitch" copper free from other impurities. It is even possible successfully to forge copper containing 1 per cent. antimony if sufficient oxygen be present.

2. In copper which has been "overpoled," antimony tends to mitigate the phenomenon of "spewing" during solidification.

3. "Tough-pitch" arsenical copper (0.4 per cent. arsenic) is slightly hardened for hot-rolling by the presence of antimony (0.2 per cent.), but, otherwise, its mechanical properties are slightly improved.

4. The mechanical properties of "tough-pitch" pure copper after rolling and annealing are but little altered by small additions of antimony. The tensile strength is slightly raised,

and the elongation is lowered. The slight gain in toughness is probably traceable to the greater soundness of the cast ingot.

5. With regard to the structural condition of antimony in "tough-pitch" copper, it exists in two forms:—

(a) Partly in solid solution (probably as dissolved Cu_3Sb).

(b) Partly as an insoluble compound with oxygen (slate-coloured "oxidules").

Oxygen in excess exists as cuprous oxide (light-blue "oxidules"). The latter, together with the antimonial "oxidules," form a ternary eutectic with the solid solution.

6. The addition of *lead* to pure copper or arsenical copper causes the surface of a "tough-pitch" ingot to sink during solidification. Further poling with the object of obtaining a level surface is attended by the risk of rendering the metal "red-short." Like antimony and arsenic, lead tends to check "spewing."

7. The mechanical properties of arsenical copper (0·4 per cent. arsenic) at normal temperature are little affected by the addition of lead (0·2 per cent.).

8. The addition of *tin* (0·2 per cent.) to "tough-pitch" arsenical copper is attended by an increase in hardness during hot and cold rolling, and an increase in tensile strength. The elongation is correspondingly lowered, but the toughness is unimpaired.

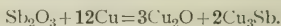
Finally, the author wishes to express his indebtedness to Mr. C. H. Eden of Messrs. Vivian & Sons, Swansea, for permission to have the ingots rolled; to Mr. W. S. I. Bray (manager of Messrs. Vivian & Sons' Works at Margam) for his interest and assistance; to Professor Arnold, D.Met., for invaluable aid in making the alternating-stress tests; and to Mr. T. G. Jones, M.Sc., Head of the Engineering Department, Swansea Technical College, for his kindness in carrying out the tensile tests on the 30-ton Buckton testing-machine in his Department.

DISCUSSION.

Professor A. K. HUNTINGTON, Assoc. R.S.M. (Vice-President), in opening the discussion, said the paper was very welcome to the members, because it dealt with a very difficult subject on which many more papers would have to be written before it was thoroughly threshed out. The author stated on page 206: "It seems to be clear that the antimony exists in the higher state of oxidation (Sb_2O_4), because in alloy VII. (Table V.), although the antimony was added in the form of antimony trioxide (Sb_2O_3), it split up into antimony—which formed Cu_3Sb , and partly entered into solid solution—and the slate-coloured constituent already described." Personally he took exception to that statement, because he did not believe for a moment that it was possible to have a higher oxide of a metal present in the presence of the copper. He had always believed, and still believed, that in such a case the copper would reduce the antimony to the lowest possible oxide, and that Sb_2O_4 would not be formed under those conditions. The author assumed that some of the antimony could be combined with the copper, and that that enabled the rest to form a higher oxide. That seemed to him to be quite an untenable position. With regard to the experiments generally the author had been working on the question of what would roll and what would not roll. That was a perfectly legitimate proceeding, but the uses of the copper must not be lost sight of. It was no good being able to roll a copper if it could not be put to practical use afterwards. One of the principal uses of copper was for locomotive boiler plates and stays, and it was certain that some of the products which the author had succeeded in making would be of no use at all in a boiler. The author had stated that in the alternating tests some of the specimens behaved very differently from what they did under ordinary tensile tests. It was possible to carry that very much further. He believed he was correct in saying that all the tests were made cold, but it must be borne in mind that in a locomotive boiler they were not working in the cold; far from it. If the metal that the author tested by alternating stress was unsatisfactory cold it was absolutely certain it would be very much more unsatisfactory hot. In many cases where a very fair result was obtained in the cold with an alternating stress, an absolutely bad result would be obtained at a comparatively low temperature, say 400° to 500° F. Those were a few points which had to be taken into consideration in reading the paper. One must not run away with the idea that because a thing could be rolled it had any practical use. There were many other points to which he might allude, but he would not deal with them at the moment.

Dr. C. H. DESCH (Glasgow) said there were a number of points in the paper that were open to considerable discussion, but he proposed to confine his remarks to only one or two of them. With regard to the chemical action mentioned on page 207, he was quite in agreement with Professor Huntington that the equation there given was impossible.

That copper should behave as an oxidizing agent, raising antimony from a lower to a higher valency, was not in accordance with anything known in chemistry. He thought the following equation would meet the purpose :—



The copper behaved as a deoxidizing agent; and the copper would take oxygen away from the antimony in that particular case. With regard to the interpretation of the structures, they were told that a ternary eutectic was formed, two of the constituents of which were oxidized. To infer the existence of a ternary eutectic without making a thermal analysis was quite an unjustifiable proceeding. Ternary eutectics were formed, but only under certain conditions of equilibrium which could be determined thermally. There was no evidence of that in the paper, neither did the photomicrographs indicate anything like a ternary eutectic. With regard to the globules which showed two constituents embedded in the metal, the probable explanation seemed to him to be a very much simpler one than that given by the author. It appeared to him to be a case of mechanical entanglement, the globules being like portions of a liquid phase entangled as in an emulsion. The structure was in accordance with photographs of that kind published by Guertler. In previous discussions the question had been raised of the influence of oxygen on those alloys—as to whether the oxides were capable of forming to some extent solid solutions with the metals. That point was not mentioned in the paper, although it had been raised several times at previous meetings, and was one that required some investigation. One was apt to assume offhand that the oxides must necessarily appear as separate constituents; but that a certain quantity of oxygen might actually go into solid solution was not beyond the bounds of possibility, and that would explain some points which were not quite clear. He thought many of the members would have something to say with regard to the properties of the metal. He would only say in that connection that an element such as antimony, which might be made harmless if a perfect balance were maintained between it and the oxygen, but which in the absence of that quantity of oxygen was exceedingly dangerous, was a thing that most manufacturers would not care to have in their works. There were too many chances of accidents happening, and from one's ordinary knowledge of the disastrous effect that antimony had on copper, he thought it would be wiser to avoid it if possible.

Dr. T. K. ROSE (London) said that although it was quite obvious that such a chemical equation as that given on page 207 could not happen, the one that Dr. Desch had just put forward could not happen either. In such a case there must be a division of the oxygen between the metals. If only one irreversible action were possible, then it was much more likely that antimony would reduce oxide of copper than that copper would reduce oxide of antimony. But he felt no doubt that if antimony, copper, and oxygen were heated together it would be found that oxide of antimony, oxide of copper, and antimonide of copper

all occurred in the final product. The exact proportions could not be predicted, and could only be determined by careful measurement.

Professor T. TURNER, M.Sc. (Honorary Treasurer), thought that it would be a good thing carefully to test the reaction to which several of the speakers had referred, and the members would then be able to see how the equation went. It was quite easy to put the constituents together, say in an evacuated tube, and see how the reaction went on. In a case of that sort there was no doubt that a little experimental evidence was much better than theoretical considerations. He was very much interested in the results given in the paper on the influence of antimony, and in the general conclusions arrived at by the author, that apparently under suitable circumstances the qualities of copper were not adversely affected by the presence of quite a large amount of antimony. He remembered the time when it was considered that arsenic seriously deteriorated copper, and copper which contained arsenic was condemned. Makers and users had learnt that arsenic was sometimes a good friend. He remembered years ago having to do with a copper locomotive firebox which proved very unsatisfactory. On analysis 0.02 per cent of antimony was found in the sample, and it was agreed both by the buyer and seller that that was a sufficient explanation of the imperfection of the copper, and the metal was replaced. So that it was considered, at all events at that time, that quite a small quantity of antimony was sufficient to deteriorate the metal. Apparently they were now going through the same phase with regard to copper as that through which they went a number of years ago with reference to cast iron. The idea then was that if the best cast iron was required it must be as pure as possible—nothing but carbon and iron. It was gradually discovered that silicon and phosphorus were an advantage; in fact every element that could be added, if it were added in suitable quantity, could be employed advantageously. Apparently much the same could be said of copper. There was no really good copper and no really bad copper: it was necessary to consider the question of the purpose for which the copper was to be employed; and by suitable additions the copper might be improved, even by an element apparently so unpromising as antimony. It was urged that difficulties would arise through having antimony in a copper works because of the influence of scrap. But a similar kind of argument was once urged in connection with steel works when it was pointed out that many kinds of cast iron were the better for phosphorus; but in some steel works non-phosphoric metal was specially required; and it was considered dangerous to have any material of a different character on the place. It was all a question of care, and it was for the particular manufacturer to consider whether or not it was advisable to run the risk. He believed copper works had to comply with a larger variety of specifications than any other kind of metal works, and therefore there was a greater chance of error. He could, therefore, quite understand that, even though antimony might sometimes be an advantage so far as physical properties were concerned, the danger would exist of it being added when it was not required.

He thought everybody would go so far as to say that, in nine cases out of ten, the presence of antimony would certainly be detrimental rather than beneficial.

Mr. LEONARD ARCHBUTT (Member of Council) said that, although he did not wish to discuss the paper, he desired to express his thanks to the author for having brought such an interesting and important subject before the Institute. As representing large users of copper, he had been convinced from the analyses he had made of locomotive copper during many years past that the small quantities of bismuth and antimony found in commercial copper could not always be so injurious as some of the text-books had led them to believe, and he thought the author had done great service in showing that there was some basis for that opinion. He quite agreed with Dr. Desch that, as the conditions under which these elements were free from injury depended upon the presence of the proper quantities of oxygen and arsenic, it was not desirable that manufacturers should depart from their previous practice of keeping copper as free as possible from bismuth, antimony, and other elements which could be so injurious under certain conditions. The paper would be very valuable to those who had to investigate causes of failure, in showing exactly in what way the elements could be injurious, and enabling one to form a better opinion as to whether the failure was due to their presence or not.

Professor H. C. H. CARPENTER, M.A., Ph.D. (Vice-President), said the equation on page 207 was likely to become famous in the discussion. A variety of objections had been expressed by the members on that point, the reason for which in his opinion was that they did not know the ternary equilibrium of copper, antimony, and oxygen. That had to be determined before any of the structures could be interpreted. He thought the author could not possibly wish his explanation to be regarded as the final one; he believed he had already stated that in introducing the paper. Certainly the matter was more complicated than Professor Turner indicated by saying that all that would have to be done was to try the particular reaction indicated in the equation. It meant working out definitely a portion of the ternary diagram for copper, antimony, and oxygen; and any one who had worked out a ternary diagram knew the enormous labour it would involve. But it would have to be done, sooner or later.

Dr. WALTER ROSENHAIN (Member of Council) said that he desired to make one remark in reference to what Dr. Carpenter had said, namely, that in connection with similar enclosures of oxidized, and, in the present case, sulphurised bodies in steel exactly the same difficulties occurred; and the steps which were being taken to investigate that matter were exactly the ones that Professor Carpenter indicated. It was found that the globules of non-metallic matter were very often exceedingly complex; they contained all the eutectics among themselves, and their explanation was by no means simple.

The PRESIDENT thought the experiments the author had undertaken were of very great value. Unfortunately they had been conducted on small ingots where the rolling was not so severe as was usually the case on a large scale. He desired to ask the author whether he had been able to persuade any of the copper manufacturers to work a 10 or 15-ton charge for him.

Mr. JOHNSON replied in the negative.

The PRESIDENT understood that the copper the author experimented with was electrolytic copper.

Mr. JOHNSON said that that was so.

The PRESIDENT, continuing, remarked that that seemed to him to be a weak point in the paper, because the author himself admitted that the effect of antimony on electrolytic copper might be—in fact, was—different from the effect of the metal on ordinary commercial copper. What the members really desired to know was what was the effect of antimony on the copper of commerce, say, on “best select” copper. Many years ago he had considerable experience with antimonial copper containing from about 0.1 to 0.05 of antimony. Difficulties did not present themselves in the hot rolling, *i.e.* in breaking down the castings, but complaints from the rolling-mill were made, when they came to the cold rolling, that the metal was hard, and when they proceeded to flanging the plates showed a tendency to crack. There was nothing else present except 0.1 and sometimes only 0.05 of antimony to cause this behaviour of the copper. With regard to the laboratory scale of the experiments, it was well known that it was absolutely necessary to begin in the laboratory, and therefore the author was to be commended for the work he had done. It was generally impossible to persuade any copper works manager to work a big charge containing a metal which was likely to injure the copper. In the seventies he was dependent for his supply of copper chiefly on Chili bar, and there was one brand, “Lota,” that was always preferred in the rolling department because it rolled so well. He found on examination that that copper contained 0.15 per cent. of arsenic after refining, and it was the arsenic that gave it its rolling properties. He was therefore led to make some experiments in the laboratory on the effect of 0.2, 0.3, and 0.5 per cent. of arsenic on refined copper, and obtained most excellent results. But nevertheless it was impossible to get an arsenical charge worked. It was admitted that the copper forged well, but the manager of the works would not risk spoiling a 10-ton charge of copper by putting in another metal which was believed to have injurious effects. That was exactly what might be expected with regard to antimony, as one of the speakers in the discussion had remarked. It would be impossible for a considerable time, certainly until many more laboratory experiments had been made, to get a charge of copper worked and treated as in ordinary practice by passing it through the rolling or the tube-drawing departments. He desired to ask the author what

grounds he had for assuming that 0·1 per cent. of antimony was beneficial to arsenical copper, say in a firebox-plate. Judging from his experience of the effect of antimony on best select copper, he would be afraid that arsenical copper containing 0·1 per cent. of antimony would show weakness in the flanging. There was another point in the paper on which he wished to ask a question, namely, the overpoling of electrolytic copper. Was the "spewing" or "spitting" due to SO_2 or not? He had had considerable experience in melting down electrolytic cathodes, and in many cases he had found that the metal in the crucible would boil and SO_2 would be given off. He had hence been wondering whether in the metal that the author had experimented with the gas that was given off was SO_2 or not. From a consideration of the manner in which the cathodes were prepared it was quite reasonable to expect that in some cases sulphur would be present, because the copper was deposited in a strong solution of copper sulphate. The cavities in the cathode might hold small quantities of that solution, and when the cathode was melted up the copper sulphate was dissociated and SO_2 was produced. In fact, with regard to the presence of copper sulphate in cathodes, he had on several occasions been compelled to advise that, before a large consignment of electrolytic copper was used for brass making, it should first be passed through the ordinary refining furnace. He most emphatically considered that the author's experiments were of very great value indeed, and they only possessed the disadvantage he had already pointed out, that they were made not with commercial but with electrolytic copper. So far as lead was concerned, he had had considerable experience in Japan with some thousands of tons of copper, which was extremely pure except that it contained lead. On examining the copper which was used by the copper workers in that country for hammering up a small cake of copper into a large and extremely thin utensil, he found it always contained about 0·25 per cent. of lead. He would not say that such copper was the best for rolling, because hammering and rolling had not the same effect on metals, as every one knew who had to do with the metals on a large scale; but with that percentage of lead in the copper the Japanese relied upon being able to hammer it up into a thinner vessel than when less was present. He only hoped that the author would be able to induce some manufacturer to give antimonial copper a trial on a commercial scale.

Mr. JOHNSON, in reply, said that Professor Huntington raised the objection to the possibility of the existence of antimony in the higher oxidized form after being added in the form of the lower oxide. His answer to that was that to pure copper antimony trioxide was added; nothing else was allowed to get into the copper, and no external reducing influence of any kind was allowed to operate. The copper was afterwards examined, and it was found that there were free areas of Cu_3Sb , and there were a number of slate-coloured oxidules which could not have been Sb_2O_3 because they had parted with some of their antimony to form the Cu_3Sb . Whether those slate-coloured oxidules were Sb_2O_4 or not he was not going to argue at the moment, but they

certainly were a higher oxide than the oxide originally introduced. Professor Huntington had mentioned the fact that although copper could go through the rolls and successively survive the severe treatment of the rolls it did not necessarily indicate that that copper would be of good service in situations where it was going to be submitted to high temperatures. All he could say in reply was that if the copper could be rolled hot, and if it would successfully go through the cold tests to which it was going to be submitted by the modern engineer, then that copper was good enough for anything. Dr. Desch had suggested an alternative reaction to the one he (the author) gave on page 207. That was a point that it would be perhaps as well to discuss after giving the subject a little more attention. As far as he could see, the reaction suggested by Dr. Desch might possibly be an intermediate one. Perhaps there might be an intermediate reaction in which Cu_2O was momentarily formed, but certainly the final one did not produce Cu_2O . In the copper to which he had already referred there was no Cu_2O existent at all. Dr. Desch also remarked that the existence of the ternary eutectic had not been definitely established. That might be the case, for he had had no means in his laboratory at the time of conducting thermal analyses, but he would stick to his guns as far as the existence of the eutectic was concerned until it was definitely disproved. The micrograph certainly showed a eutectic surrounding a solid solution, the eutectic having three definite constituents. Then Dr. Desch went on to suggest that if an element was present which was likely to cause a manufacturer to wrinkle his brows occasionally it was as well to keep it out. Other speakers had dwelt on that point to some extent. Personally he thought that any manufacturing firm which could not look after its scrap—which could not keep the different kinds of scrap in different compartments—was rather lacking in organization, and very simple organization at that. Professor Turner suggested carrying out experiments with the addition of the elements in an evacuated tube, but Professor Turner had already proved himself that antimony was volatile *in vacuo*. Antimony in copper would volatilize when heated *in vacuo*, and that would upset the experiment.

Professor TURNER thought that would not be the case if it was exactly in the quantities the author had given. He did not suggest investigating the whole question, but simply that particular reaction.

Mr. JOHNSON, continuing, said he desired especially to thank Mr. Archbutt for his remarks. They came from a man who had considerable knowledge of wrought copper in its various forms, and the fact that experiments of the kind dealt with in the paper were appreciated by Mr. Archbutt was sufficient reward in itself for all the work that had been carried out. Professor Carpenter suggested that experiments should be carried out to determine the ternary system, and went on to say that such work would be very laborious. Professor Carpenter had shown such great ability in carrying out the determination of ternary systems that it would be folly for him (the author) to trespass on his special

preserve, so that he could safely leave the determination in the hands of Professor Carpenter. Dr. Rosenhain mentioned the complex character of the non-metallic impurities in metals. That was decidedly the case with copper. He could not give the exact composition and constitution of some of the non-metallic impurities, because even the slate-coloured oxidules to which he had given some attention differed considerably in themselves. Some of them looked just as though they had held cuprous oxide in solution at a high temperature, and precipitated it later on. Others showed no signs of any precipitation, but were merely slate-coloured areas without any definite structure at all. In reply to the President's remarks, it was his ambition to work experimental charges containing impurities on a commercial scale. That would undoubtedly be in some respects more advantageous than carrying out experiments on a smaller scale. He had, however, sufficient experience with small scale experiments carried out in combination with large scale experiments to know, from the point of view of forged copper, that if small ingots would forge hot it might be taken for granted that large ones would do so also. The President had rather decried the use of electrolytic copper for the experiments.

The PRESIDENT said he did not say that. What he said was that it was a disadvantage, because it was necessary in all experiments of the kind to start first of all with the pure material.

Mr. JOHNSON said the President had in the last remark he had made answered his own question; he was driven to the use of electrolytic copper. There was no single recognized brand of commercial copper. If one particular brand of commercial copper were taken, somebody would say that it was not like the commercial copper he had been dealing with; that it contained other impurities in different quantities. There were thousands of various brands of commercial copper on the market. So that if brands of commercial copper were used it would multiply enormously the number of experiments that would have to be made. The President attributed to antimony a more harmful influence on the cold working properties of the copper than on its hot working properties. That was the case; it would harden the copper for cold rolling, but in his own experiments he found it did not have any serious effect. No edge cracking was produced. It was possible that the copper which the President mentioned could have been rolled with a little more care with regard to the amount of reduction, or it was possible it might have contained a trace of something else. It probably was not analysed for oxygen. He was familiar with the "Lota" brand to which the President had referred, and knew that at one time at any rate it was a good brand.* With regard to the presence of sulphur in electrolytic cathode copper, he had already proved in previous experiments that cathode copper undoubtedly contained sulphur, but if, as the President suggested, the

* The author had subsequently referred to some old analyses and found that the "Lota" brand contained cobalt to the extent of 0.4 per cent. in some cases.

copper was first put through a refinery the sulphur would be practically eliminated. That was exactly what was done in the present case. The electrolytic copper was melted down, surcharged with oxygen, and converted into "set" copper before bringing it up to the "tough-pitch" stage. There was in the crucible first of all copper which had been surcharged with oxygen, so that sulphur dioxide could not possibly exist, and that was poled up until nothing was left but oxygen and gases.

The PRESIDENT said that sulphur dioxide was more soluble in copper saturated with cuprous oxide than it was in pure copper. A copper which was set-pitch always contained a considerable amount of sulphur dioxide, but when it was worked up to tough-pitch out came the sulphur dioxide.

Mr. JOHNSON said his answer to that was that the object of working copper to the "set" condition was to get rid of the excess sulphur dioxide.

The PRESIDENT said it was not got rid of altogether.

Mr. JOHNSON, continuing, said that in dealing with the question of the influence of lead the President mentioned that utensils were made containing 0.25 per cent. of lead. In that case there was probably enough oxygen present to enable the copper to survive the mechanical treatment; in his case there was not sufficient oxygen present to enable it to survive hot rolling (see Ingot L2, Table VII., page 209).

The PRESIDENT was sure the members would agree with him that they had listened to an extremely interesting paper from Mr. Johnson, and that it deserved their most hearty thanks.

The resolution of thanks was carried with acclamation.

COMMUNICATIONS.

Mr. JOHNSON, in continuation of his remarks made during the discussion of his paper at the meeting, wrote in further reply to Dr. Desch that the latter's explanation of the occurrence of the "oxidules" in copper as being due to mechanical entanglement was not the correct one. There would be as much justification in stating that cuprous oxide was mechanically entangled, whereas, as was well known, it occurred as the constituent of a eutectic. Dr. Desch could rest assured that oxygen did not enter into solid solution. When as little as 0.01 per cent. was plainly discernible under the microscope, it might be taken for granted that any smaller quantity than that, even if it did exist in solid solution, which was extremely doubtful, could affect neither the properties of the metal, nor the validity of the author's statements.

In attempting to discredit the case which the author had made out

for the usefulness of antimony in certain limited quantities, Dr. Desch had made an unfortunate choice. The author could assure him that if his (Dr. Desch's) recommendation to avoid the use of an element because it required careful balancing with oxygen were observed, then the refining of "tough" copper would become a lost art, since it was just that careful balancing between impurities and oxygen which had enabled refiners to produce millions of tons of good commercial copper. There were other reasons why Dr. Desch's recommendation possessed no value, and they were as follows:—

(1) Impurities were most useful in "tough" copper, which had to be raised to high temperatures in service, since they enabled it to retain the hardness conferred by the rolls or draw-bench in situations (*e.g.* steam-pipes) where electrolytic copper would become completely softened.

(2) Impurities helped copper to resist corrosion.

(3) Impurities such as arsenic and antimony were cheaper than copper itself.

(4) Even if the author had not held a brief for the *addition* of antimony, his experimental proof of its harmlessness in certain proportions was reassuring, since antimony frequently occurred in crude bar copper, and its removal entailed considerable expense.

(5) Finally it was known to the author that antimony was often *added* to charges of commercial "tough" copper with beneficial results.

Referring again to the equation on page 207, which Dr. Desch considered to be an impossible one, the author, after further consideration, could not entertain the possibility of the alternative reaction suggested by Dr. Desch, for the simple reason that Cu_2O was not a product of the reaction.

Referring again to the remarks of the President, the author was most interested in the statement that sulphur dioxide was more soluble in "set" copper (copper saturated with oxygen) than in copper up to pitch. The author was aware that the operation of poling tended to eliminate SO_2 if resorted to *prior* to the "set" stage, *i.e.* in working "blister" to "set" copper. Any such influence was, of course, due to the mechanical agitation of the bath, and to the more thorough exposure to atmospheric oxidation. So far as his experience went—and he was confirmed by others*—the solubility of gases (including sulphur dioxide) was at a minimum in "set" copper. The removal of oxygen raised the solvent power of the copper for gases. All this, however, did not affect the author's contention that electrolytic copper could be spoilt and rendered porous by "overpoling." The author would like to point out the difference between the terms "tough" and "tough-pitch." The term "tough" was usually employed for impure copper (containing arsenic) which was generally manufactured into tubes, firebox plates and stays, &c. The term "tough-pitch" was employed to describe any brand of copper which had been brought up to pitch in the refinery; for instance, one could have "tough-pitch" electrolytic copper. In fact all commercial copper which had been refined was or ought to be in the "tough-pitch"

* Hofman, Hayden, and Hallowell.—*Transactions of the American Institute of Mining Engineers*, vol. xxxviii.

condition, whereas the term "tough" was only applied to arsenical "tough-pitch" copper.

Mr. H. GARLAND (Cairo) wrote with reference to the determination of oxygen in copper, inquiring whether Mr. Johnson had, at any time, compared the microstructures of the same piece of copper before and after the removal of the oxygen? Some difficulty would no doubt be experienced in preparing a polished surface if the metal were in the form of thin sheet or foil, but, as Mr. Johnson had pointed out in a previous paper,* Archbutt had determined the oxygen in a solid cylinder of copper $\frac{1}{2}$ inch in diameter, so that it ought to be possible to examine the sample microscopically both before and after the oxygen analysis.

The writer desired to know where he could see photomicrographs such as these, and supposed that the specimen after reduction would be more or less pitted according to the oxygen content?

Mr. J. L. HAUGHTON, M.Sc. (Birmingham), wrote that Mr. Johnson's paper was an admirable example of an investigation by a man who combined a scientific training with a thorough knowledge of what manufacturers wanted. He was particularly interested in the explanation of the condition in which antimony was held to exist in tough-pitch copper, and also the effect of small quantities of tin on arsenical copper. The latter experiment seemed to indicate that it would be well worth while to carry out a systematic research on this subject.

Mr. H. Y. YOUNG (Wallsend-on-Tyne) wrote that on page 199 the author invited discussion upon the merits of the distillation method for antimony in copper. The writer's experience was that the method gave so much trouble that even if it could be proved reliable it was not worth the doing. Personally he separated the antimony by the same method as the one Mr. Johnson described, using oxalic acid instead of sulphuric acid when the presence of tin was suspected.

Mr. JOHNSON wrote in reply to Mr. Garland's communication that he had compared the microstructures of pieces of copper before and after the removal of oxygen. The sheet copper presented great difficulties in preparing sections for the microscope, but these were overcome by mounting the section on pieces of wood by the aid of some adhesive material. The difference in the structure after annealing in hydrogen lay in the appearance of the areas formerly occupied by light blue cuprous oxide, these merely appearing black; also cracks appeared between the enlarged crystals when the original percentage of oxygen was high. He would refer Mr. Garland to Mr. Archbutt's paper † for photomicrographs of copper before and after deoxidation in hydrogen. He wished to thank Messrs. Haughton and Young for their communications, and was interested to learn that Mr. Young had had experience similar to his own in the antimony determination.

* "The Effect of Silver, Bismuth, and Aluminium upon the Mechanical Properties of 'Tough-Pitch' Copper containing Arsenic," *Journal of the Institute of Metals*, No. 2, 1910, vol. iv. p. 233.

† *The Analyst*, vol. xxx., No. 357, pp. 385 *et seq.*

THE INFLUENCE OF OXYGEN ON THE PROPERTIES OF METALS AND ALLOYS.*

BY E. F. LAW, ASSOC. R.S.M. (LONDON).

FOR some years the author has been urging the necessity of a fuller recognition and appreciation of the influence exerted by oxygen when present in metals and alloys; but that the subject has not received the attention which it deserves is evident from some remarks recently made by Sir Gerard Muntz. During the discussion on a paper by Hughes† before the Institute of Metals, Sir Gerard Muntz said: "There was one other point which must not be lost sight of in the study of the question—unfortunately it was generally lost sight of—namely, the question of oxygen. As far as his experience went he did not think the importance of that point had sufficiently, or at all, come home to the practical man—he would not include his scientific brethren, because one never quite knew what was in their minds; but the practical maker of metals, and more especially the practical users, had not given half enough consideration to the value of the comparison of the proportionate amount of oxygen to the other ingredients."

And again, during the discussion on a paper by Greaves‡ on the copper arsenic alloys, the same gentleman said that "he desired to impress upon the engineering world, especially his friends in the railway world, the great importance of the question of arranging the oxygen content when they specified the arsenic content, because if they did not take any notice of the oxygen, it was not much good their taking any notice of the arsenic."

In view of the importance attached to the influence of

* Read at Autumn General Meeting, London, September 26, 1912.

† "Non-ferrous Metals in Railway Work," *Journal of the Institute of Metals*, No. 2, 1911, vol. vi.

‡ "The Influence of Oxygen on Copper containing Arsenic or Antimony," *Journal of the Institute of Metals*, No. 1, 1912, vol. vii.

oxygen by so eminent an authority on copper and its alloys, it occurred to the author that a useful purpose might be served by bringing forward the question before the Institute of Metals, with the object of raising a discussion which might lead to further study and a more complete understanding of the subject. It must be clearly stated at the outset, however, that the present paper does not claim to be in any way a complete study of any particular metal, but is written rather with the object of reviewing the relations of metals with their oxides from a broad and general standpoint.

Metallic oxides may be regarded as the natural or stable condition of existence of nearly all the metals. From these oxides the metals are won by the expenditure of energy, and they are themselves, therefore, in the nature of combustibles, and will tend to revert to their former condition with the liberation of energy. Both in the winning and working of metals unceasing care has to be exercised in order to prevent oxidation, and the difficulties attending the successful accomplishment of this object have been overcome by the practical man with little assistance, it must be admitted, from the scientist. As the result of experiment, he has found that the addition of certain substances improves the quality of the resulting metal, and without fully understanding the true reason of the improvement, he has succeeded in presenting us with a formidable list of deoxidizers. Following the introduction of phosphorus in 1853 came manganese and aluminium, and within the last few years, silicon, magnesium, cadmium, vanadium, titanium, and boron, both singly and in combination with one another. It is true that some of the metals mentioned form useful alloys, but in many cases their sole function is to deoxidize the metal to which they are added. So important is the deoxidation of metals and alloys, that it would probably be no exaggeration to say, that when the history of the alloy industry comes to be written the record of progress during the last twenty years will be summed up in the words, "the use of deoxidizers."

In spite of its importance, however, the scientific side of the question has been almost entirely neglected. No doubt this is partly due to the experimental difficulties attending the

determination of oxygen, and it is true that one's sympathies would naturally be extended to the unfortunate metallurgist who was asked to determine the oxygen in an aluminium alloy; but it is the business of the scientist to overcome difficulties, and if it can be proved (as it certainly can) that oxygen exerts a powerful influence on the properties of metals, then he must be prepared to give the subject his serious attention. A chemical analysis of copper, for example, which failed to report 0.1 per cent. of lead would be regarded as, to say the least of it, unsatisfactory, and yet it not infrequently happens that ten times this quantity of cuprous oxide, which is in many cases a much more injurious constituent than lead, is passed over without notice in the reported analysis. This is surely unscientific and illogical. Moreover, the omission is more serious than it appears at first sight, because the oxides, having lower specific gravities than the metals, occupy a larger volume, and it must not be forgotten that the influence exerted by an impurity depends upon its volume and not upon its weight. Those who are unaccustomed to the examination of commercial metals and alloys would be astonished at the large volume of non-metallic matter which frequently finds its way into their composition without being indicated in any way by the chemical analysis.

Judging from those cases which have been examined, it would appear that metallic oxides (and we are not concerned here with occluded oxygen but only with combined oxygen) are insoluble, or practically insoluble, in metals and alloys. They occur as particles, varying in size and distribution, entangled and embedded in the metal, and it is obvious that the existence of these non-metallic particles scattered throughout the metal must seriously affect its properties. One or two examples will perhaps serve to illustrate these points. Fig. 1 (Plate XXIX.), for example, is a polished and unetched section of a portion of a bearing bronze taken from a rolling-mill. The photograph is not taken of a specially selected portion, but represents a fair average sample of the alloy. To all outward appearance the metal was satisfactory and was put into service, but it is not surprising that it had to be removed after only two hours' work, owing to excessive heating. Whether in

bronze or white metal bearings the presence of oxide will invariably cause trouble.

Figs. 2 and 3 (Plate XXIX.) are taken from a section of a locomotive firebox which fractured in service. This fracturing of oxidized arsenical copper has had attention drawn to it by Bengough and Hill* in their very valuable paper on the copper arsenic alloys. The complete analysis of this sample showed the following results:—

Copper	99.349
Arsenic	0.433
Lead	0.009
Nickel	0.056
Oxygen	0.115
Bismuth	trace
Antimony and sulphur	nil
	<hr/>
	99.962

This is an excellent example, both of the excessive amount of oxide which is sometimes found in commercial alloys, and also of the large quantity of oxide represented by a relatively small figure in the analytical results.

While dealing with the copper alloys of this type it must be pointed out that they occupy a somewhat unique position in regard to their relations with oxygen, and in view of their great industrial importance it may not be out of place to consider them briefly.

Three papers have recently been read before the Institute of Metals dealing more or less with the properties of these alloys, and while in no way wishing to minimize the importance of the valuable work contained in these papers, it must be confessed that a perusal of them, together with the discussions which took place at the time of their reading, leaves the mind of the reader in a state of considerable confusion as to the real nature of the alloys and the impurities which exert such a prejudicial influence. Bengough and Hill, for example, consider that the oxygen in copper arsenic alloys occurs as arsenious oxide, while Huntington suggests that it exists in the form of a copper arsenite. On the other hand, Johnson† declares that it exists as cuprous oxide, and goes so far as to state that arsenious oxide is reduced by metallic copper with

* *Journal of the Institute of Metals*, No. 1, 1910, vol. iii.

† *Ibid.*, No. 2, 1910, vol. iv.

the formation of cuprous oxide. Frequent reference is made to the eutectic of copper and cuprous oxide, which, in all the photographs reproduced, is conspicuous by its absence; and even as regards the manufacture of the alloys, the old theory that arsenic behaved as a deoxidizer has been abandoned, and some declare that it is immaterial whether the arsenic is added in the form of arsenious oxide or metallic arsenic. It is difficult, however, to find any justification for a method of procedure which deliberately adds an element which is not wanted, and must be subsequently removed if the quality of the metal is not to suffer. An additional difficulty in the way of a clear understanding of these alloys is due to the fact that published determinations of oxygen are in most cases altogether unreliable. Errors of two and three hundred per cent. are by no means uncommon.

The peculiarities which have placed these alloys in a unique position and have been the cause of so many conflicting views are, firstly, the fact that copper forms a simple series of alloys with its oxide; and secondly, that the heats of formation of cuprous and arsenious oxides are both low, and do not differ widely from one another. Hence the oxides do not form very strong combinations, but are easily reduced to the metallic state; whereas copper and arsenic combine to form one of the strongest and most clearly defined of the intermetallic compounds. The result of this is that not only is the arsenic incapable of acting as a deoxidizer, but, even if present in an oxidized condition, is actually reduced more or less completely, and combines to form arsenide of copper, which passes into solid solution. If copper arsenite were formed it would immediately rise to the surface, as it is an easily fusible compound. There is as little likelihood of copper arsenite being entangled in an arsenical copper as there is of phosphate of copper occurring in a phosphor-bronze.

It is interesting to note that copper containing arsenide in solution does not form the characteristic eutectic structure of copper and cuprous oxide. The oxide occurs in the massive form. This is not an isolated instance, as Hudson and the author have shown * that in the case of phosphor-copper the

* *Journal of the Institute of Metals*, No. 1, 1910, vol. iii.

eutectic structure completely disappears if the copper contains a small quantity of tin in solution. It is obvious, however, that the physical and mechanical properties of the alloys are materially affected by this change in structure.

A series of alloys has been prepared, showing the effect of increasing additions of arsenic to oxidized copper, and some of the more interesting of the photographs which have been taken of these alloys are reproduced and will serve to illustrate the changes taking place in the structure. In making these alloys, best electrolytic copper was used, and was oxidized in the crucible—no addition of oxide being made. The requisite quantity of arsenic was added in the usual way and a small ingot cast after each addition. Fig. 4 (Plate XXX.) shows the oxidized copper. The eutectic composition has purposely been exceeded, and dendrites of cuprous oxide are seen embedded in the eutectic. Fig. 5 (Plate XXX.) is the same sample at a higher magnification, and shows the characteristic eutectic structure of copper and cuprous oxide. Fig. 6 (Plate XXX.) shows the appearance of the alloy after a small addition of arsenic. A breaking up in the continuity of the ground mass of eutectic will be observed; and Fig. 7 (Plate XXX.), at a higher magnification, shows the way in which this takes place by the "balling up" of the particles of oxide. In making up this sample a content of 0.075 per cent. arsenic was aimed at, and the analysis showed 0.078 per cent. It will be noticed that even in the presence of an excess of cuprous oxide this small quantity of arsenic enters into solution as arsenide. Fig. 8 (Plate XXXI.) shows an intermediate stage in the process of gradual coalescence of oxide particles, with increase of arsenic, until in the sample represented by Figs. 9 and 10 (Plate XXXI.) the eutectic structure has completely disappeared. In this case the saturation point of arsenide in copper has just been exceeded, and free arsenide is beginning to separate out. Fig. 11 (Plate XXXII.) shows the same sample after etching, the free arsenide occurring as minute dark particles in the lighter coloured solid solution.

It will be seen, therefore, that although there are certain peculiarities connected with the occurrence of oxide in arsenical copper, it does not differ from other alloys in its susceptibility

to oxidation or in the mode of occurrence of the oxide. The presence of the arsenic in no way hinders the oxidation of the copper.

The mode of occurrence of oxides in metals is naturally of great importance. As regards mechanical tests the minimum effect is produced when the oxide occurs in massive form, as in the case of the arsenical coppers just considered. Figs. 12 and 13 (Plate XXXII.), taken from an etched sample of a locomotive firebox, show that the oxide does not necessarily occur between the crystals, although it sometimes happens that they lie on the boundary of two crystals.

The maximum effect is produced when the oxide occurs as a network between the crystals, as shown in Fig. 14 (Plate XXIX.), which is taken from an oxidized sample of a "special" bronze. In reality, however, this is not nearly so serious (at any rate from the user's point of view) as the previous example, because the defect is usually made apparent by the poor mechanical tests; whereas the whole trouble with oxidized metals is that they frequently pass the mechanical tests, and only when they are put into service does the real trouble begin.

The work of Bengough and Hill with reference to the fracture of oxidized copper arsenic alloys by reducing gases has already been referred to, and the author has shown* that the blisters produced in the pickling of thin steel sheets previous to tinning, and the fracture of hard steel under similar conditions, are both due to the reduction of oxide in the steel. Doubtless there are other cases which might be mentioned, but it is in connection with the subject of corrosion that the question is of the most vital importance.

During the last few years innumerable papers have been written on the subject of corrosion, and every imaginable influence assisting the rate of corrosion (even to the action of sunlight) has been pressed into the service of the enthusiastic investigator, until the unfortunate user, if he were ever inclined to take these papers seriously, must have given up the problem in despair long ago. Interesting as all these scientific investigations may be, there is a tendency to overlook one point of

* *Journal of the Iron and Steel Institute*, No. I. 1906, vol. lxxiii. ; and No. II. 1907, vol. lxxvi.

view, and that happens to be the point of view of the practical man. It cannot be too strongly urged that the difficulties which beset the users of metals and alloys are not so much those of uniform and normal corrosion. These are more or less in the nature of known factors, and can be made the basis of calculations. It is the cases of abnormal corrosion—pitting and local deterioration, in most cases due to the presence of non-metallic impurities—which upset all calculations and cause so much trouble. Whereas theories regarding the nature of electrolytes and the differences of potential between the constituents of alloys have been discussed at great length, the author cannot recall a single instance in which an analysis of the material investigated has included a figure for oxygen, or even suggested its presence. Nor do there appear to be any determinations of, or even references to, the differences of potential between metals and oxides, in spite of the fact that they far outweigh the relatively small differences existing between the separate metallic constituents of alloys. Here we are not dealing with millivolts but with measurements of far greater magnitude, and as an illustration of the practical utility of the difference of potential between a metal and its oxide we need go no further than the ordinary electric accumulator. It is the more surprising that this subject has not received more attention, considering that the injurious effect of imperfect protective oxide coatings is well known and has been studied at some length. In the case of steel the influence of oxide has received slightly more attention; but by no one has it been more fully realized than by Mr. C. P. Sandberg, for whom the author has carried out a number of tests. Plates of ordinary steel, and plates of the same steel rolled from ingots which have been deoxidized by the addition of silicon, have been exposed to the London atmosphere for more than three years, and have been carefully cleaned, examined, and weighed at intervals of six months. The results have shown that the rate of corrosion of the ordinary plates is 24 per cent. greater than that of the deoxidized plates; or, in other words, the life of the deoxidized steel as shown by these tests is 24 per cent. longer than that of the ordinary steel. Under normal conditions of service this figure would be exceeded,

because the artificial removal of the oxide every six months exposes a fresh surface, and the plates start corroding under the same conditions. Under ordinary circumstances the more corrodible plates would scale more frequently than the less corrodible ones, a fresh surface being exposed each time to the full action of the corroding agents. This effect has been observed in the case of experimental plates, which have been exposed for more than six months without cleaning, and in which automatic scaling has taken place.

Another example which may be mentioned of abnormal corrosion due to oxide is to be found in the case of oxidized welds, which have been described in some detail by Merrett, Digby, and the author.*

From the evidence which is constantly coming under his notice, and of which this paper is an attempt at a brief summary, the author is firmly convinced that experiments on corrosion which omit to take into account the presence of oxides in the metals experimented upon are of little value; and that in practical work it is equally important that the presence of oxides, whether introduced during the manufacture or subsequent treatment of the metal, should be considered. The manufacturer has found that the greater fluidity and superior qualities due to freedom from oxide are matters of great moment both in the casting and after treatment of the metal; but the user has not yet realized that from his point of view a perfectly deoxidized metal is of equal, if not greater, importance.

* *Journal of the Iron and Steel Institute*, No. I. 1911, vol. lxxxiii.

DISCUSSION.

Professor A. K. HUNTINGTON, Assoc.R.S.M. (Vice-President), in opening the discussion, said the author had brought his (the speaker's) name rather prominently forward in the text of the paper. For instance, he said on page 225: "Huntington suggests that it exists in the form of a copper arsenite"; and on page 225 the author said: "If copper arsenite were formed it would immediately rise to the surface, as it is an easily fusible compound. There is as little likelihood of copper arsenite being entangled in an arsenical copper as there is of phosphate of copper occurring in a phosphor-bronze." He was afraid he did not at all agree with the author in that statement. In discussing a previous paper read at the Institute—he believed it was Messrs. Bengough and Hill's—he made some remarks which he specially took the trouble to say were in no way to be taken as dogmatic; in fact, he actually used the term. He said he had no wish to dogmatize about the existence of that arsenite, or to assert that what he had stated was the case, but that was the impression he obtained from the work he carried out at the time, and the probabilities appeared to be in favour of that view. He submitted that that was a fairly humble way of putting it, and in no way dogmatic. At the same time he saw no reason from any evidence adduced by the author to alter his impression. The author had given some very good photographs, which he (Professor Huntington) fully appreciated, but the interpretation of those photographs was altogether another matter. The author had his interpretation; he (the speaker) had his. There was no evidence that the author was right; there was no evidence at the moment that he (Professor Huntington) was right. At the same time, there was no evidence that he was wrong, and he saw no reason whatever why his view of the position should not be correct. The copper and the arsenic would, to his mind, undoubtedly combine with oxygen rather than with one another as metals, and the oxides would further tend to combine together to form an arsenite. In the experiments he made there was distinct evidence that there was something quite different to oxide of copper; that that something had been dissolved in the copper, and was segregated round the boundaries. It had not completely segregated, as he pointed out at the time, but if heat had been applied for a longer time there would have been a complete segregation of the body. He would not labour the point any further at the moment. As he said a few minutes ago, in dealing with another paper, he thought there was a great deal of work yet to be done on the point, and he welcomed the author's contribution as a step in the right direction.

Dr. WALTER ROSENHAIN (Member of Council) said that he was afraid he would disappoint the author by saying that he approved of everything he had said in the paper. The paper touched on a matter which the author was perfectly right in suggesting had not received the amount of attention which it deserved. The whole question of non-metallic matter in metals, beginning at steel at one end and going right through

the metals and alloys to platinum, where no oxides were obtained, was one of extreme difficulty but also of extreme importance. He thoroughly agreed with the author's views that progress in regard to those metals and alloys was a matter of getting rid of the impurities, and understanding them in the first place with a view to getting rid of them. There were two or three points to which he wished to refer. First of all, the author stated in one place what he did not quite mean, where he said that the oxides were not soluble in metals as a rule. He took it, the author meant solid metals, because there was evidence that oxides were soluble in molten metals in some cases. That had been proved in the case of copper by Heyn. The question of the solubility of oxides in metals was an extremely difficult one to determine, and the only way to do it—and perhaps it also was the only way in which to determine the amount of oxygen present in a metal—was by the depression of the freezing point. That sounded a little bit awkward from the point of view of the analytical chemist, but the best way to determine the oxide would be accurately to determine the freezing point of the substance; to note the effect of each and all the separate impurities present, and to note what difference was due to the oxygen. It was again a method by difference, which, however, he believed was capable of a great deal of accuracy, because the depression of the freezing point could be very readily ascertained. That was a possibility, because they had to determine the depression of the freezing point in a given metal by oxygen alone. He was engaged in trying to do that at the present moment in the case of iron, and if the method worked there he hoped it would be possible to apply it to other things. That was a possible way of advance in that direction. Another possible method of getting at the result desired was by volatilizing the metal and leaving the oxide behind. In some cases the oxide was as volatile as the metal, but in others it was not. In aluminium that was the only hope, to volatilize the metal and leave the oxide behind. That he thought played a vital and important part, as every one who had dealt with the material must realize. A certain amount of work had been done by Heyn on the question of the manner in which the oxygen behaved where another metal was added, but the author had not referred to it in the paper. Heyn, in his work on the action of tin, found that non-deoxidized bronzes contained crystals of oxide of tin. In that case there was no copper oxide left whatever, and the whole of the oxygen went to the tin. In other cases it was probable that the solubility of the two oxides came in, because although the oxides might not be soluble in the solid metals they were soluble in one another in the solid state. With regard to the interpretation of the photographs by the author, they were an example of what such things ought to be, and he very much wished that other photographs of non-metallic impurities were of the same high order. Their interpretation had been advanced considerably by the work of a Russian investigator, Matweef, who worked on the impurities of steel with a view to obtaining methods for determining their nature by microscopic reaction. The method, which Mr. Humfrey and himself (Dr. Rosenhain) used before that Russian investigator, consisted of heating

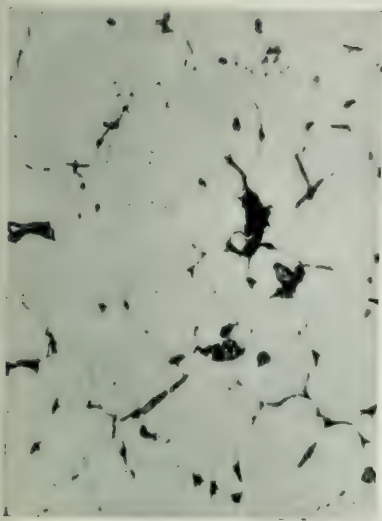


FIG. 1.—Bearing Bronze.
Magnified 100 diameters.

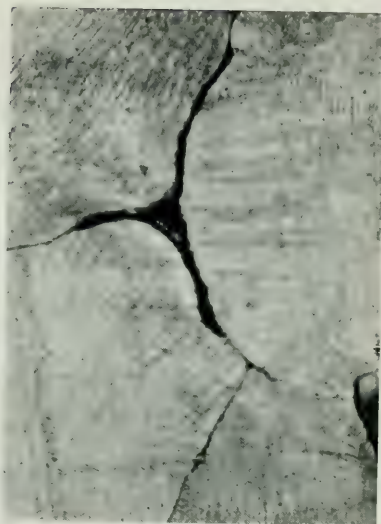


FIG. 14.—Oxidized Bronze.
Magnified 1000 diameters.

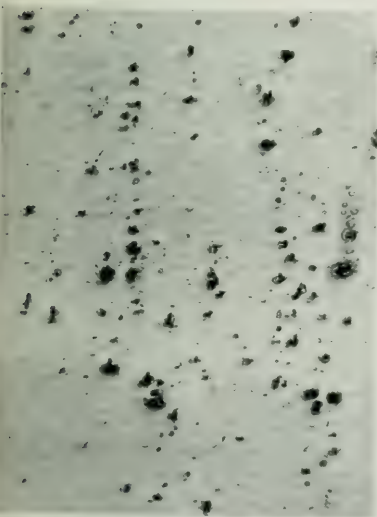


FIG. 2.—Locomotive Firebox.
Magnified 100 diameters.

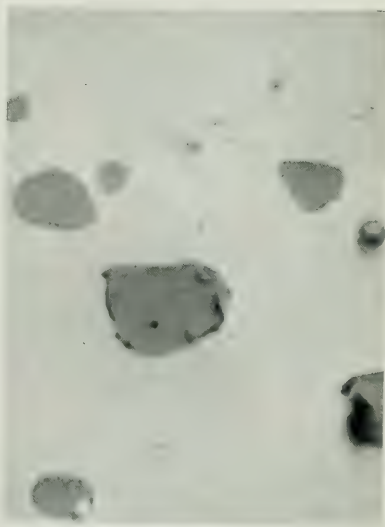


FIG. 3.—Locomotive Firebox.
Magnified 1000 diameters.

(Vertical illumination.)

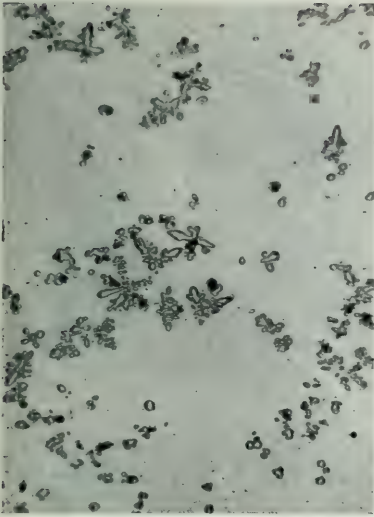


FIG. 4.—Oxidized Copper. Dendrites of Cuprous Oxide in Eutectic. Magnified 100 diameters.

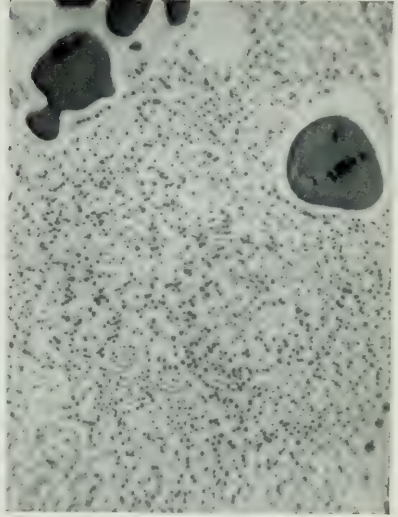


FIG. 5.—Oxidized Copper. Eutectic. Magnified 1000 diameters.

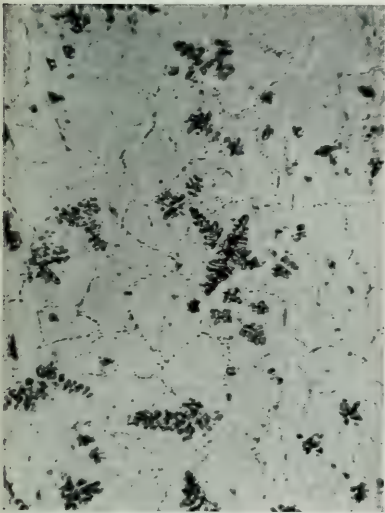


FIG. 6.—Same as Fig. 4, but containing 0.078 per cent. Arsenic. Magnified 100 diameters.

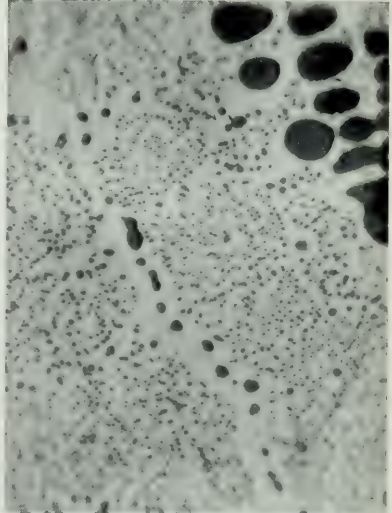


FIG. 7.—Same as Fig. 6. Magnified 1000 diameters.

(*Vertical illumination.*)

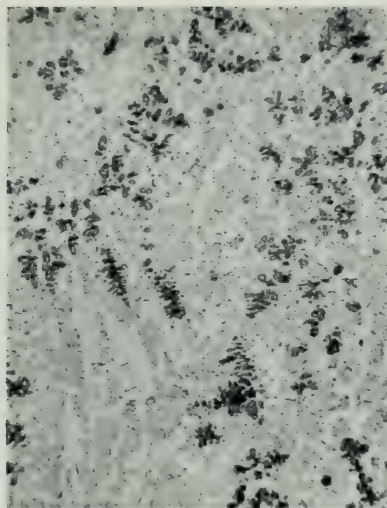


FIG. 8.—Same as Fig. 4, but containing
0.42 per cent. Arsenic.
Magnified 100 diameters.

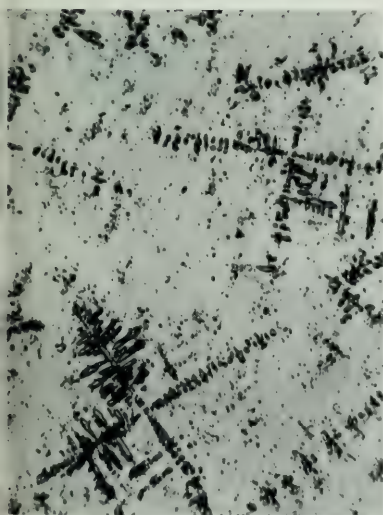


FIG. 9.—Same as Fig. 4, but containing
2.28 per cent. Arsenic.
Magnified 100 diameters.

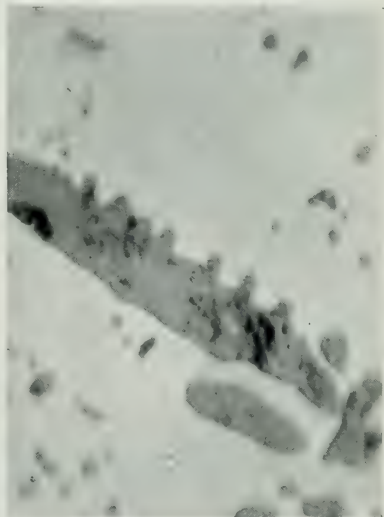


FIG. 10.—Same as Fig. 9,
Magnified 1000 diameters.

(*Vertical illumination.*)

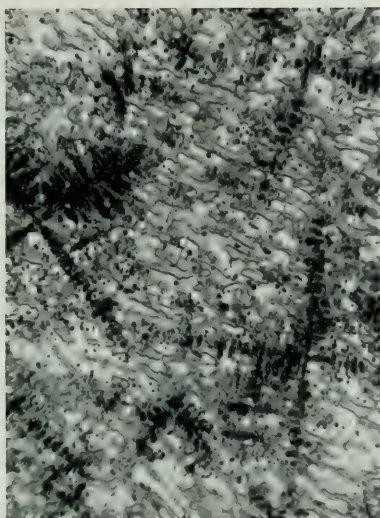


FIG. 11.—Same as Fig. 9, but Etched.
Magnified 100 diameters.

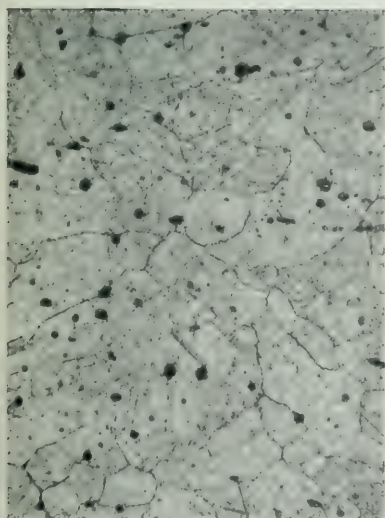


FIG. 12.—Firebox Copper, Etched.
Magnified 100 diameters.

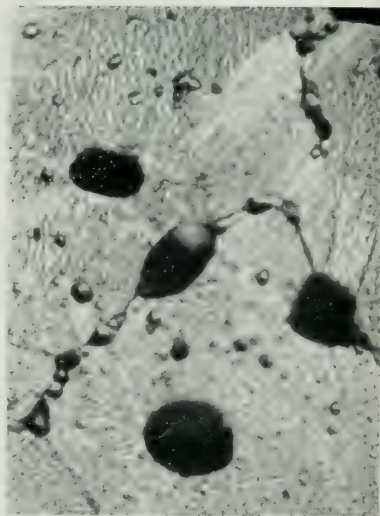


FIG. 13.—Firebox Copper, Etched.
Magnified 1000 diameters.

(Vertical illumination.)

the polished etched specimen in a current of hydrogen, and seeing which of the impurities were reduced. It was not a pleasant sort of thing to do with a polished and etched specimen, but it was possible, and once the gas was obtained pure enough it worked very nicely. He thought some of Professor Huntington's difficulties in interpreting the photographs might be met by gaseous etching of that kind.

Mr. F. JOHNSON, M.Sc. (Birmingham), said the statement was made on page 224 of the paper: "A chemical analysis of copper, for example, which failed to report 0.1 per cent. of lead would be regarded as, to say the least of it, unsatisfactory, and yet it not infrequently happens that ten times this quantity of cuprous oxide, which is in many cases a much more injurious constituent than lead, is passed over without notice in the reported analysis." He thought the statement that cuprous oxide was ten times more injurious than lead was open to objection.

Mr. LAW, interposing, said he thought Mr. Johnson had misread the paper. It simply meant ten times the amount.

Mr. JOHNSON, continuing, said even ten times the quantity was not so injurious as that much of lead.* The non-rolling properties of the specimen he showed earlier in the morning were due to the presence of lead and the absence of oxygen. Had the oxygen been there the copper would have been good copper; it was the lead which ruined it, and not the oxygen. On pages 224 and 225 the author referred to the presence of oxide in bronze; and in Plate XXIX. Fig. 4 he showed an oxidized bronze. He wished to ask whether that bronze was analysed for oxygen. On page 225 the author referred to the excessive amount of oxide sometimes found in commercial copper, and gave a tabulated analysis of an arsenical copper. He wished to put in a plea for the manufacturer. So long as commercial brands of crude copper came into this country other than electrolytic so long was the manufacturer driven to introduce oxygen into his copper to counterbalance the influence of impurities, and 0.11 per cent. could not be regarded as an excessive amount of oxygen. It possibly might have been reduced a little more than that, but the point was that the oxygen must be there, and it could not be regarded as an element which must be got rid of at any price; it had to be there in a certain small quantity. He agreed with the author that if that quantity were much exceeded trouble would arise. The author referred on the same page to a paper † which he (Mr. Johnson) read, in which he had maintained that oxygen existed in an arsenic-copper alloy as cuprous oxide, and he thought the author's experiments went to confirm that statement. In the discussion on that paper he (Mr. Johnson) had exhibited a photomicrograph, showing just the point which Mr. Law had brought out so much more clearly by the aid of much better photo-

* The speaker referred, of course, to copper containing 0.1 per cent. lead and no oxygen, as compared with "tough-pitch" copper containing 1.0 per cent. Cu_2O (0.11 per cent. O).

† *Journal of the Institute of Metals*, No. 2, 1910, vol. iv.

micrographs. His own photomicrograph was printed on ordinary paper, and did not show up quite as well, but it showed the separation of the cuprous oxide dendrites, and the appearance of the α -solid solution and the Cu-Cu₂O eutectic, all three appearing quite separately from one another, just as they appeared in Fig. 8, Plate XXXI., of the author's paper.

Dr. C. H. DESCH (Glasgow) said that, like Dr. Rosenhain, he was in almost complete agreement with everything the author said. He thought the paper would prove most valuable because it suggested a number of most important problems that awaited solution. He desired to make a few remarks with regard to the phenomena observed on adding arsenic to copper containing oxide, and the progressive changes in structure, which were shown in the excellent photomicrographs, consisting of the gradual disappearance of the eutectic structure and the appearance of a homogeneous ground mass with distinct dendrites. He suggested that there was not an actual disturbance of the condition of equilibrium, but rather that the addition of the arsenic increased perhaps the liability to under-cooling; and that the structures from which the eutectic was absent were really structures which, according to the equilibrium diagram, should be free from eutectic, but were under-cooled structures; that, owing to the presence of the arsenic, under-cooling went on to a further extent, and free dendrites were obtained instead of a eutectic. It was a kind of thing that occasionally happened in metals, and was extremely frequent in igneous rocks, where eutectic structures were rare on account of the liability to under-cooling. That was often affected by the addition of a new constituent, which went into solid solution. It was possible that arsenic might play that part, and in that case the progressive series of changes would not represent a change in equilibrium. The point which he mentioned in the discussion on Mr. Johnson's paper bore, perhaps, rather on Mr. Law's work—as to the possibility of the existence of solid solutions of the oxides in metals. He gathered from the paper that the author still had an open mind on that subject, and that he did not deny the existence of solid solutions. It was a point which certainly required investigation. There were suggestions from the microscopical evidence that such solid solutions might occasionally be formed. The main difficulty in that kind of investigation seemed to be the practical impossibility of getting good analytical estimations of oxygen in the alloys. He suggested that the author, with his great analytical experience, might perhaps be able at some time to devise methods for that purpose. The methods at present available were quite unsatisfactory. The methods just suggested by Dr. Rosenhain might perhaps be practicable at the National Physical Laboratory, but for those who had to put up with much less complete equipment he was afraid that separating the aluminium from its oxide by distillation was not at present an easy analytical operation.

Mr. T. VAUGHAN HUGHES, Assoc.R.S.M. (Birmingham), said that Professor Huntington had given in the course of his paper on "The

Effect of Temperatures Higher than Atmospheric on Tensile Tests of Copper and its Alloys," certain results likely to be obtained in practice. He showed in his paper precisely what the engineer encountered under circumstances of stress at temperatures above the normal atmosphere. The author's paper was also of great practical importance, because he had taken trouble to exhibit, by means of prints from photographs at high magnification, the actual state obtaining in a metal between the crystal boundaries and the crystals themselves. The import of his research was of great moment to the user of non-ferrous metals. What was the present state of affairs in the preparation of metals and alloys? Great pains were taken to deoxidize the metals and alloys, often by adding small quantities of deoxidizing impurities to them in order to enhance their mechanical properties. Then, in course of further manufacture, they were subjected to unnecessary maltreatment. They were raised to high temperatures in air; they were permitted to be in contact with hot oxygen; very often hot oxygen was blown upon them; and thus the very ingredient in regard to which most attention was paid in removing it from the original metal or its ore was again added over extended surfaces in subsequent operations. For that reason he had given the subject a close attention. One fact had been clearly proved to members of the Institute, *i.e.* it was most necessary and imperative that great and continued care should be taken to prevent the subjection of metals between process to hot oxygen or air treatment in course of manufacture, or, at any rate, to the least possible extent. It was impossible, unless one could apply on a large practical scale methods such as those having experimental significance, referred to by Dr. Rosenhain, of operating *in vacuo*, to prevent the access of oxygen, a difficult proposition to advance at present although applied in the glow lamp industry. But when cold work was applied to metals during manufacture, it was quite possible to take precautions from the beginning to the end of operations to exclude oxygen in the heat-treatment process. For that reason and others, the subject-matter of the author's paper was deserving of the greatest attention, and was of supreme practical importance. The allusion the author made to the lead accumulator and corrosion was one which all the members ought to keep constantly in mind.

Dr. T. K. ROSE (London) said his mind had been a little perturbed by the statement on page 224 of the paper, that metallic oxides were practically insoluble in metals. He believed that metal oxides were, in some cases at least, dissolved in metals, forming solid solutions. The author spoke all the way through his paper as if oxygen were a sort of general malefactor; that sometimes it went undetected, but if ever it was found it must be pursued and captured at all costs. But in the case of gold it was entirely different. There they did not fear the oxygen at all; in fact they put as much oxygen as they could into the gold. The trouble they experienced was with tellurium and bismuth, and these were got rid of by means of oxygen. He had supposed for years that oxide of lead up to say 0.01 or 0.02 per cent. actually

dissolved in the standard gold. At any rate, when they had oxidized the lead and made the gold tough, then by annealing in a reducing atmosphere it became brittle again.

Mr. O. F. HUDSON, M.Sc. (Birmingham), asked the author if he had any experience in the detection of oxides in brass, particularly rolled brass. Were oxides present in serious quantity in such brasses?

Mr. LEONARD ARCHBUTT (Member of Council) quite agreed with the statements contained in the paper. He thought the author had done valuable service in calling attention to the presence of non-metallic impurities in metals, especially in the papers he had read before the Iron and Steel Institute. It was astonishing, when one had to examine a large number of steels under the microscope, as he had to do, to see the amount of disseminated particles of sulphide, slag, or other non-metallic matter that was frequently present. Although he agreed with the importance of the paper, and thanked the author for again calling attention to the subject, he did not think the illustrations given were all very convincing; at any rate, not without further explanation. For instance, the author stated on page 224: "Those who are unaccustomed to the examination of commercial metals and alloys would be astonished at the large volume of non-metallic matter which frequently finds its way into their composition without being indicated in any way by the chemical analysis"; and then in Plate XXIX. he gave a photograph of a bearing bronze. That looked to him like an unsound casting full of holes; and if that unsound portion occurred on the seat of the bearing, and particles of grit got into the holes, the journal would be scored and the bearing would run hot. Perhaps the author would say in his reply whether the dark areas really represented non-metallic impurities. If that was the case, it was a shockingly bad casting. Then again, he did not think the author's analysis of the firebox plate on page 225 was very convincing as an example of a defective plate, because he could assure the author that it was no uncommon thing to find more oxygen than that in firebox plates which went into service and gave a good life. It might not be desirable that oxide particles, such as those shown on Plate XXIX., should be there, but they were there and were very generally there; and he had seen much worse cases than that of fireboxes which had gone into use and not cracked. He was not apologizing for the presence of those particles, but he did not think, without further explanation, he would like to say that that particular firebox cracked because it contained 0.115 per cent. of oxygen. On page 226 the author said that errors of 200 and 300 per cent. were by no means uncommon. Did he really mean that when determinations of oxygen were being made, the analyst reported 0.1 per cent., when there might be 0.3 per cent. present, or *vice versa*; or were the figures in the paper a misprint for 2/100 or 3/100 per cent.? If they were a misprint for 2/100 or 3/100, he agreed; but if it was the case that the errors might amount to 200 or 300 per cent. it was very alarming; and he hoped the author would say in his reply what was the method that gave those exceedingly

erroneous results, and would also indicate a method which gave more accurate results.

The PRESIDENT said that all who had to deal with metals with the exception of gold, as Dr. Rose had pointed out, regarded oxygen as a malefactor, except in one case, *i.e.* in tough-pitch copper, where it must be present in proper quantities.

Mr. LEONARD ARCHBUTT said the President had asked for further remarks with reference to the influence of oxygen on corrosion. He intended in his previous remarks to have referred to the fact that the author did not mention the influence of sulphur. He did not know whether the sulphide of manganese in steel had not perhaps as great, if not more, influence on corrosion than oxygen might have. The author rather seemed to lay stress on the oxygen being the cause of the corrosion, and he did not mention sulphur at all.

Mr. E. F. LAW, Assoc.R.S.M. (London), in reply, said that Professor Huntington seemed to think that he (the author) had taken some remarks of his as being rather dogmatic. That was not the case. The words he used in his paper were "Professor Huntington suggests," so that he thought he had put it quite mildly. Then Professor Huntington did not quite agree with the conclusions that he (the author) had come to from the photographs he had shown. Professor Huntington still adhered to his experiments and the conclusions he drew from them, and he (the author) adhered to his, so that he was afraid they had reached a deadlock. He did not see how the difficulty was going to be solved, and they must agree to differ. He was glad to know that Dr. Rosenhain agreed with him in most of his contentions. He was fairly certain that he would, because those of the members who had to examine metals after they were put into service must be convinced of the importance of the non-metallic impurities. Dr. Rosenhain had referred to the fact that he had used the words "the solubility of oxides in metals" in the paper; and he had corrected him by saying that he should have said "in solid metals." That was the case; he was not referring in any way to metals in a liquid condition. The determination of oxygen by chemical methods was a most difficult matter. Dr. Rosenhain's suggestion of volatilizing the metal and leaving the oxide was, he thought, rather Utopian. It might be done in some cases, but they were working with small quantities of impurity in such large masses of metal that he thought it presented very serious difficulties. With regard to the question of reduction in gas and what had been called the microchemical examination, he was convinced that that was their strongest line of research, and for years he had been working in that direction. There was no doubt that by submitting polished sections to the action of gases most valuable information could be obtained, and many of his conclusions had been based on the results so obtained. Mr. Johnson had raised the question of lead being more injurious than oxide, and objected to his statement that oxide was more injurious than lead. Personally he was convinced that it was. Where

they differed was that Mr. Johnson was probably referring to tests on the metal immediately after it was made; whereas he (the author) referred to tests on the metal some time after it had been made—the actual breakdowns in service; those mysterious fractures and troubles which constantly occurred, and which were due to oxide. That was why he said it was so injurious, because oxide very often did not show itself on the mechanical tests of metal after it was made. It was in the conditions of service that it showed itself, and it was then that the disasters occurred.

Mr. JOHNSON asked to be allowed to interpose a remark with reference to the analysis of Dean on the firebox plate. In one of the early Reports of the Alloys Research Committee into Firebox Plates there was one showing a large percentage of lead which had a very long life indeed.

Mr. LAW understood that Mr. Johnson was attributing the harmfulness to the lead and not to the oxide; that he blamed the lead more than the oxide.

Mr. JOHNSON said that was so; he thought it was more serious.

Mr. LAW said that he blamed the oxide more than the lead, so that he was afraid they must differ on that point. Dr. Desch had raised a very interesting question with regard to the effect of arsenic on the oxide eutectic, and suggested under-cooling. That was a very interesting suggestion and a possible explanation, but whether it was the true explanation or not he did not feel in a position to state. With regard to the solubility of oxides in metals, he thought it was unreasonable to believe that oxides to a certain extent were not soluble in metals, but all the evidence showed that if they were soluble it was only to a very limited extent. Possibly there were some metals whose oxides were soluble, and which had not come under his observation; but in most cases he thought the solubility of oxide must be very small. Dr. Rose had raised a question on the existence of lead oxide in gold. That was, he admitted, a very interesting point. The question of the brittleness of gold had been a subject of research for a great many years past. About every ten years a research was made on brittle gold, but whether they had got to the bottom of the subject yet he did not know. He thought Dr. Rose could say more about that question than anybody else; personally he admitted that he had not studied the question. Mr. Hudson had asked him whether he had any experience of oxide existing in ordinary brass. He had had very considerable experience of it, and he thought in brass it was very often distinctly injurious, more especially with regard to corrosion. The corrosion of brass tubes was in very many cases due to oxide. Mr. Archbutt desired to know whether the photograph in the paper was of an unsound casting or whether it was of an oxide. There was no doubt that it was oxide. He was only able to show a single photograph, and that naturally presented a difficulty to Mr. Archbutt, who had not had an opportunity

of examining the samples themselves. He had made an immense number of photographs, but naturally the Secretary would consent to the reproduction of only a limited number; and even then a photograph, however carefully it was reproduced, only showed a small area, and never gave the same idea as was obtained from a systematic examination of the specimen. Mr. Archbutt might take it from him that it was a case of oxidation. With regard to the determination of oxygen in copper, he was afraid he had touched there on rather a sore point with Mr. Archbutt. The figure stated in the paper was not erroneous; he had made the statement quite deliberately after consultation with Sir Gerard Muntz, who, he was sorry, was not present at the meeting. He had some correspondence with Sir Gerard Muntz on the question of oxygen in copper, and in his (the author's) letter to him he said that his experience was that if the decimal point was shifted they got at somewhere near the truth. He asked Sir Gerard for his opinion, and Sir Gerard agreed with him. He thought in many cases what he had stated was the fact. There was sometimes too great a desire to get a figure; they would accept a figure rather than any other evidence, even although the figure was 100 or 200 per cent. out.

Mr. ARCHBUTT said that Sir Gerard Muntz's figures for oxygen in copper, namely, about 0.02 and 0.002 per cent., always struck him as being exceedingly low. He thought that Sir Gerard Muntz must be referring to a different kind of copper; he did not think he could be referring to copper made in the refinery, which always contained much larger quantities of oxygen than those given by Sir Gerard Muntz. He thought it must be crucible copper which had been deoxidized with phosphorus. Personally he was sure errors did not exist of 200 per cent.

Mr. LAW said he thought it must be admitted that in many cases the published determinations of oxygen were very wide of the mark, and in his own experience where he had checked them he had found that to be the case.

The PRESIDENT said the author had given an exceedingly interesting paper, with which, speaking generally, he was in agreement. He was sure it would be the wish of the members to give the author a hearty vote of thanks for his excellent paper.

The resolution of thanks was carried by acclamation.

COMMUNICATIONS.

Mr. L. ARCHBUTT (Member of the Council) wrote that he had looked up the analyses of copper firebox plates supplied by different makers during the last eight years and had found that the majority of those

which he had analysed for oxygen contained 0.10 per cent. and over. Some makers usually kept the percentage of oxygen below 0.10; others more often than not exceeded that proportion. The percentage of oxygen in 130 plates was as follows:—

Oxygen.	No. of Plates.	Per Cent. of Total.
Below 0.10 per cent.	52	40.0
0.10 to 0.14 per cent. inclusive . . .	67	51.5
0.15 to 0.16 " " . . .	8	6.2
0.17 to 0.22 " " . . .	3	2.3
Totals	130	100.0

These remarks applied to refined copper containing arsenic. He thought Sir Gerard Muntz in his remarks on Mr. Greaves' paper* must have been referring to a different class of copper, melted in crucibles and deoxidized with phosphorus. He had found in such copper about the percentage of oxygen mentioned by Sir Gerard Muntz, his (Mr. Archbutt's) figures ranging from nil up to 0.023 per cent.

Dr. G. D. BENGOUGH, M.A. (Liverpool), wrote that he much regretted that he had been unable to be present at the meeting, and to take part in the discussion of Mr. Law's interesting paper.

On page 226 (last paragraph) the author said, "copper containing arsenide in solution does not form the characteristic eutectic structure of copper and cuprous oxide." He agreed with that statement of fact, but he had interpreted it rather differently from Mr. Law. He had taken it to mean that cuprous oxide had been reduced and arsenious oxide formed. In the paper by Mr. Hill and himself† they had given illustrations of oxides like those of Figs. 4 and 6 (Plate XXX.), but had considered them to be arsenious oxide rather than cuprous oxide. The idea was that arsenious oxide was not soluble in molten copper and formed no eutectic with it, and so formed massive crystals. Mr. Law seemed to reject the idea that there was any arsenious oxide present in copper at all. His own idea was that part of the arsenic was present in solution and part as oxide, the partition coefficient depending on the conditions of time and temperature. Usually there was also a small amount of cuprous oxide present. As to the importance of the presence of oxides in the general sense, he was quite in accord with Mr. Law.

He much admired Mr. Law's beautiful series of photomicrographs. With regard to Fig. 7, Plate XXX., he would like to know how much *excess* arsenic had been added to produce a *content* of 0.078. Might not some of the dots arranged in a row diagonally across the photograph be arsenious oxide, rather than balled-up cuprous oxide? It seemed to him

* *Journal of the Institute of Metals*, No. 1, 1912, vol. vii. p. 239.

† *Ibid.*, No. 1, 1910, vol. iii. opposite p. 69.

that Figs. 6 to 10, Plates XXX. and XXXI., might be interpreted to mean that as the arsenic was increased in quantity it reduced more and more of the cuprous oxide, forming crystals of arsenious oxide; some of the arsenic would of course remain in solution to give the appearance shown in Fig. 11, Plate XXXII. No doubt Mr. Law had considered that hypothesis and seen good reason for rejecting it; he put forward the suggestion in a very tentative manner.

He entirely agreed with Mr. Law's remarks (at the top of page 229) on the necessity of investigating the causes of severe local pitting. The difficulties in the way of the experimenter were, however, very great, and it was much easier to carry out the kind of work which Mr. Law deprecated. He had been engaged for many months on some experiments along the very lines suggested by Mr. Law on the last two pages of the paper, and had encountered many unexpected difficulties. He was afraid that he must himself plead guilty to Mr. Law's indictment on page 229, for he was investigating the corrosion of brasses of various kinds, but was unable to determine the oxygen in them. He ventured to suggest that even Mr. Law's well-known skill as an analyst would fail him in this matter at the present moment. If not, he felt sure that Mr. Law would earn the thanks of the whole brass world by publishing his method.

He was much interested in the result (given on page 229) of the experiments with deoxidized steel. He was himself actively engaged at the moment on experiments on the methods and results of deoxidizing brass, and hoped to communicate the results to the Institute in due course. He might add, however, that he was not yet satisfied that the presence of oxides was the most important factor in the severe local pitting which sometimes occurred in brass, but it was possibly one of several.

In conclusion, he would state that he believed that that paper, like all Mr. Law's papers, would exert a very wholesome influence by its insistence on the importance of practical problems and difficulties, and on the necessity for facing the experimental difficulties inseparable from such problems.

Mr. J. L. HAUGHTON, M.Sc. (Birmingham), wrote that, with reference to Mr. Law's statement: "There do not appear to be any . . . references to differences of potential between metals and oxides," he would like to draw the author's attention to the list of substances—including several oxides—given, in electro-chemical order, by Mr. Brühl in his paper on the "Corrosion of Brass." *

That, of course, did not in any way invalidate the author's contention that the study of the effect of oxides on the corrosion of metals had been seriously neglected, and the present paper, even were it of no value from other points of view, was most useful in emphasizing that fact.

In continuation of his remarks made at the meeting, Mr. F. JOHNSON wrote that Mr. Law's denunciation of oxygen in copper was rather un-

* *Journal of the Institute of Metals*, No. 2, 1911, vol. vi, p. 294.

fortunate in view of the fact that such material as copper firebox plates could not possibly be manufactured without it.

The whole system of manufacture, and of the purchase of raw materials, would have to be revolutionized in order to produce deoxidized copper cakes.

The tests carried out by Dean, to which the writer had referred at the meeting, went to disprove Mr. Law's statement that oxygen only revealed its evil effects after the material had been in service. The writer would take the opportunity of quoting two cases from Dean's list :—

No. of Sample.	Mileage.	Arsenic.	Lead.	Oxygen.	Remaining Impurities as Determined.	Copper.
		Per Cent.	Per Cent.	Per Cent.	Per Cent.	Per Cent.
10	441,744	0·05	0·268	0·248	0·155	99·22
13	506,341	0·29	0·126	0·174	0·124	99·25

Both these samples contained fairly high percentages of lead and oxygen, and Sample 10 could be fairly described as so rich in oxygen as to be under pitch ; yet its mileage was quite good. Sample 13 possessed more oxygen than the sample quoted by Mr. Law, but it had a mileage of over 500,000. Both samples quoted gave satisfactory tensile tests *after being in use*, viz. :—

No. of Sample.	Breaking Stress, Tons per Square Inch.	Elongation, Per Cent. on 8 Inches.
10	14·5	42·7
13	14·4	33·98

Sir GERARD MUNTZ, Bart., Past-President, wrote that he much regretted that he was prevented from being present to listen to and join in the discussion on Mr. Law's paper, which paper he considered valuable as drawing attention to a subject hitherto far too little appreciated or studied.

Some of the points made in Mr. Law's arguments were of special interest ; for instance, Mr. Law stated that metals were won from their oxides ; hence it was self-evident that the most perfect form of a metal was that from which all oxides had been eliminated. In the matter of deoxidizers, it must be evident that the best were those which did their work and left no residues in the form of alloys, or infusions of any sort, within the metal which it was desired to deoxidize.

As to the determination of the oxygen in metals and alloys, it would appear that the scientific metallurgist had yet far to go before the solution of some of the mysteries was arrived at, notably in the matter of the brasses. Nevertheless there were simple practical methods, which probably the scientist would consider too crude and unscientific for consideration, which might be worth following up ; for instance, the method of determining the amount of oxygen in copper by melting samples in

salt and estimating the oxygen contents by the difference in weight before and after so melting; might not that simple practice also be the solution of the problem of determining oxygen in brass? anyhow, it might possibly be worth the scientist's consideration.

If, as had been stated by Mr. Law, the oxides of metals were practically insoluble in metals, it must follow that their presence must tend to break up, and therefore weaken, the structures of any metal in which they were present.

Mr. Law's photographs, Figs. 2 and 3, Plate XXIX., sufficiently demonstrated what happened in that regard, and further the analysis given showed that the oxygen contents, 0.115 per cent., were far too great; for the best results to be obtained the oxygen should have been reduced to about 0.015 per cent.

As to the action of arsenic on copper, Sir Gerard was of opinion that there could be no doubt from a practical point of view that it acted as a deoxidizer, in so far that it reduced the copper oxides and absorbed the oxygen from the copper, though exactly what form it took then he would not be prepared to say; he would leave the scientist to settle that point.

From many experiments and much practice he (Sir Gerard) had been led to the conclusion that though the addition of arsenic reduced the copper oxides it did not remove the oxygen from the arsenical copper alloys.

Comparison of Mr. Law's photomicrographs, Figs. 5 and 6, Plate XXX., tended to confirm that view, and Figs. 9 and 10, Plate XXXI., carried confirmation even further, showing the removal of the eutectic structure of copper and cuprous oxide.

The well-known properties of arsenic of increasing the tensile strength of copper would probably be satisfactorily accounted for by the explanation given on page 228, paragraph 2, viz. in the production of the massive form of oxide and the reduction from the eutectic form, but to obtain the best results it would be desirable to remove the oxides as entirely as possible.

With regard to the fracture of oxidized copper by reducing gases, experiments made in the laboratories of Muntz's Metal Co., Ltd., at the French Walls Works, Birmingham, had demonstrated that the higher the oxygen content the greater the liability to "gassing." Ordinary tough-pitch copper containing 0.18 per cent. oxygen was rendered absolutely rotten, whereas specially treated copper, containing 0.015 per cent. oxygen, was in no wise detrimentally affected under precisely similar conditions.

In his (Sir Gerard's) estimation that result arose from the fact that owing to there being practically no oxygen present in the specially treated alloy, it stood to reason that the reducing flame could not reduce the oxides and thus break up the structure, and that therefore it had no effect on the metal. The deoxidized copper had very high tensile strength and elongation, and was easily worked hot or cold.

With regard to Mr. Law's suggestion that the presence of oxides might have a marked effect upon the question of corrosion, the writer was of opinion that there might probably be good ground for research in

that direction, although for the present, in the matter of condenser tube trouble, there remained the difficulty that hitherto no method of determining the amount of oxygen in brass had been arrived at; that must be the first step in the research.

Possibly, however, something might be done in the way of experimenting with brasses deoxidized by the most efficient known methods and other brasses purposely prepared with an excessive inclusion of zinc oxide, and comparing the results. The almost total dezincification of Muntz's Metal, which at times occurred in the use of that alloy in sea water, and which had hitherto never been completely and satisfactorily explained, might well be considered in conjunction with the trouble of the "pitting" of brass condenser tubes; there might probably be found to be a close analogy between the two phenomena. The dezincification of Muntz's metal was mysterious in so far that in two adjacent sheets on a ship's bottom one would be badly affected throughout and the other quite immune, though the analysis of the two sheets might show identically the same ingredients, and as far as was known both had been subject to exactly the same treatment in the course of manufacture.

What was first required was a perfectly reliable method of determining oxygen in brass.

Next, they required to know what was the effect of heat treatment, both in casting, rolling, and annealing brasses. Also, what was the different effect, if any, on brass of treating in an oxidizing or deoxidizing flame during the above-named processes?

Mr. H. J. YOUNG (Wallsend-on-Tyne) wrote that Mr. Law held the opinion that oxygen in metals and alloys had received but little attention from practical men, and quoted authorities. At the Newcastle (1911) Meeting of the Institute, however, a paper by Professor H. Louis, M.A., D.Sc., Assoc.R.S.M., on "The Failure of a Brazed Joint"* was devoted to discussing the effects of 0.4 per cent. of lead and 0.77 per cent. of tin, notwithstanding that the analysis showed "oxygen and loss" as 0.63 per cent. In a communication on that paper the writer attempted to point this out, but the published reply was that it was "quite beside the question." Attention was now drawn to it only for the purpose of endorsing Mr. Law's remarks, and of proving that practical men were accompanied by most of the theoretical ones in the present question. With some little diffidence the writer offered the view that that might sometimes be caused by too great faith in analytical methods, which at best were only as accurate as the operator and the procedure could make them, under conditions which neither might always be able to control.

The writer also wished to state his views regarding oxides and the corrosion question as discussed by Mr. Law. He had seen several copper and brass tubes with one or more definite pits or holes while the rest of the tube was perfect, and had always held the opinion that such a peculiar effect could only have been originated by some particle of oxide

* *Journal of the Institute of Metals*, No. 2, 1911, vol. vi.

being entangled in the metal at that spot. Such an opinion had helped him when considering that great mystery, for, as Mr. Law pointed out, there was indeed a difference of potential worth more consideration than that between the separate metallic constituents of a tube giving an analysis similar to that of thousands of unaffected tubes. Also it seemed more feasible than the idea that the particle had been brought along by water or other agency and had tenaciously affixed itself.

Mr. E. F. LAW wrote, in reply, that he was much gratified with the discussion which had taken place on his paper, and wished to thank all those who had contributed towards it. In his anxiety to concentrate attention on essential points he had carefully refrained from clogging the paper with descriptions of experimental work and details of observations and experiences. He did not regret the course he had adopted, but it undoubtedly had one drawback, for while it accomplished the object aimed at in preventing the discussion wandering off on side issues, it appeared to leave an impression in the minds of some that he had arrived at conclusions without any evidence whatever.

Mr. Archbutt had brought forward a number of interesting figures showing the results of his determinations of oxygen in copper firebox plates. Unfortunately he was unable to say anything about these figures, as he had not had the opportunity of comparing his results with those of Mr. Archbutt on the same sample of copper. He had no doubt, however, that Mr. Archbutt's figures were comparable, and that was a point of very great importance. With regard to the figures quoted by Mr. Johnson, he would only say that he had referred to the Report in question for details of the method employed, and the only information he could gather was that "the combined oxygen had been estimated by a method devised by Sir Frederick Abel."

He was much interested and a little amused to notice how tenaciously we clung to old traditions in spite of our scientific progress. A figure obtained by analytical methods was the only thing that would satisfy, and he had been asked by several members to devise a method for the determination of oxygen. His reply to that was that some years ago he had spent many (to him) valuable weeks determining the oxygen in steel in order to convince certain unbelievers, and he was not going to be inveigled into any such enterprise again. Modern research was only now beginning to dispel the fog of misunderstanding created by the figures of analytical methods, and yet the desire for these figures was as prevalent as ever. For his own part, he had no desire to represent these things by figures which, even if accurate, would probably be misleading. They had better and more efficient methods at their disposal.

He was glad to have Mr. Bengough's contribution to the discussion, in view of that gentleman's very important work on the copper arsenic alloys. In spite of the fact that he was not in complete agreement with Mr. Bengough on one point of relatively minor importance, he had never had any reason to modify the very high opinion which he had formed of that work at the time of its publication. When he began his work

on the copper arsenic alloys he shared Mr. Bengough's views, but as the work progressed he was gradually compelled to alter those views.

In reply to Mr. Bengough's question as to the excess arsenic added to produce a content of 0.078 in the sample represented by Fig. 7, Plate XXX., he would say that no excess was added. The calculated amount of arsenic necessary to give 0.075 per cent, was added with proper precautions to prevent loss. The difference between 0.075 and 0.078 might be accounted for in many ways, but in any case was within the limits of experimental error either in the manufacture of the alloys or in the analytical determinations. The fact that so small an addition of arsenic entered into solution (and copper containing arsenic in solution was easily distinguishable from that free from arsenic) when in the presence of such large quantities of cuprous oxide was one of his reasons for considering that arsenic united with free copper rather than with the oxygen of any cuprous oxide present. This explanation of the behaviour of arsenic was not really inconsistent with theory, for although it was true that the heat of formation of arsenious oxide was slightly greater than that of copper oxide, it must not be forgotten that the reactions which took place were not of the test-tube order and could not be represented by chemical equations. The process as he conceived it was as follows: Firstly, on adding arsenic to metallic copper it immediately melted and was distributed throughout the whole mass of metal. Secondly, there was the possibility of reaction between the cuprous oxide and *an extremely dilute solution of arsenic in copper*. Possibly in the course of time this reaction might be complete, but under the conditions of ordinary working he believed it was not. Of course he did not mean to convey the impression that the cuprous oxide in arsenical copper was chemically pure. Doubtless it contained a small and variable quantity of arsenious oxide, just as the constituent of steel known as manganese sulphide contained sulphide of iron, but there was no ground for regarding it or describing it as arsenite of copper. He hoped to have the pleasure of going fully into the matter with Mr. Bengough in order to consider the evidence; evidence which, with all respect to Professor Huntington, really did exist, and rested on a firmer foundation than the "interpretation" of a photograph by some one else.

In reply to Mr. Haughton, it was true that Mr. Brühl had given a list of substances, including oxychlorides, hydrates, oxides, and carbonates, but these were rather the products of corrosion and not impurities existing in the metal.

Sir Gerard Muntz's remarks were always of great interest and importance. He had an inexhaustible fund of practical information backed by a scientific knowledge which was none the less formidable because its existence was always denied. He (Mr. Law) was gratified to find that Sir Gerard agreed with him on the essential points. The suggestion of comparing brasses purposely oxidized with similar brasses carefully made and deoxidized was excellent and should yield most important results. He ventured to think that experimental work of this kind was much more important than any chemical methods for

determining oxygen, and he sincerely hoped that Sir Gerard Muntz would see his way to carry out those experiments, as no one was better able or better qualified to do so. With regard to the dezincification of Muntz metal, he had only a limited experience of this, but did not think that it was connected with oxidation.

He was indebted to Mr. Young for his contribution to the discussion and the confirmation of his views which it afforded. Mr. Young had expressed his own views exactly when he referred to the "too great faith in analytical methods, which at best were only as accurate as the operator and the procedure could make them. . . ."

OXYGEN IN BRASS.*

BY PROFESSOR THOMAS TURNER, M.Sc.
(UNIVERSITY OF BIRMINGHAM).

I.—OCCURRENCE OF OXYGEN.

It is generally recognized by practical men that brass may be spoiled under certain circumstances as a result of oxidation. For example, brass which has been poured at a lower temperature than usual is apt to be inferior, and this is attributed to the entanglement of oxide of zinc in the metal owing to its viscid or plastic character. It is believed that the inclusion of oxide of zinc in this way may be one of the causes which occasionally lead to rapid and irregular corrosion with condenser tubes. When sheet brass is annealed in a reducing atmosphere, dezincification may take place, owing to the volatilization of zinc; but if the atmosphere is oxidizing, a certain amount of oxide of zinc may also be produced in the alloy and rottenness result. The conditions under which such results are produced do not appear to be well understood, while the manner in which oxygen acts is generally a matter of doubt. The mode of occurrence, influence, and estimation of oxygen in brass is therefore of considerable practical interest.

It is well known that cuprous oxide is soluble in molten copper, with which it forms a eutectic with 3.45 per cent. of Cu_2O . References to standard researches on this subject will be found in the paper recently contributed to this Institute by Mr. R. H. Greaves, B.Sc.† The copper oxide eutectic is visible under the microscope and can be very plainly seen with samples of copper, which are otherwise pure, though the eutectic becomes more or less obscured as the proportion of impurities increase. Zinc oxide, on the other hand, does not appear to be soluble in zinc, nor can either cuprous oxide or zinc oxide be detected by any characteristic appearance in brass of ordinary good quality.

* Read at Autumn General Meeting, London, September 26, 1912.

† *Journal of the Institute of Metals*, No. 1, 1912, vol. vii. p. 218.

The presence of oxygen has not been recorded in the gases extracted from brass when heated in a vacuum.

The question therefore arises as to the form in which oxygen can exist in brass, assuming it to be really present. In order to ascertain whether copper oxide can exist in the presence of zinc, it is only necessary to perform a simple experiment. If powdered black oxide of copper be mixed with finely divided zinc in equivalent proportions, and heated in a test tube, it will be found to react readily with the evolution of heat, and the product consists of metallic copper and oxide of zinc.

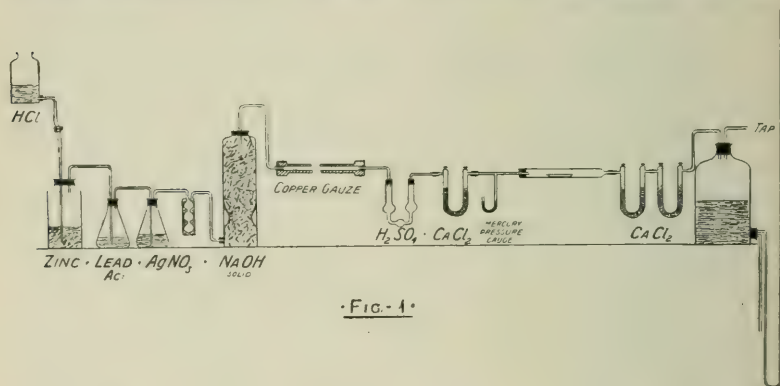
The converse experiment of heating zinc oxide with finely divided copper has been carefully tried in my laboratory by placing the mixture in a porcelain boat in a vacuum and heating to the melting point of copper. If any reduction occurred there should be a corresponding loss of metallic zinc by volatilization, but our experiments show that no appreciable loss occurred. Hence, though zinc reduces copper oxide to metallic copper when the materials are heated together, copper does not reduce oxide of zinc.

From this it is evident that copper oxide cannot possibly exist dissolved in brass, as it would be immediately decomposed when the alloy was melted. The only oxide which can exist would appear to be oxide of zinc, and this might conceivably be either in solution or in suspension. So far as I am aware at present there is no evidence to prove that oxide of zinc can dissolve in brass any more than that it can dissolve in zinc itself; nor is there any microscopic evidence of the separation of oxide of zinc in brass either as a eutectic or in any similar form. We are driven, then, to the conclusion that any oxide of zinc that may be present is mechanically entangled, and when it has any effect upon the microscopic structure it is represented merely by minute holes in which it originally occurred, but from which it has been removed during the processes of polishing and etching.

II.—ESTIMATION OF OXYGEN.

The usual method of estimating oxygen in copper is that

introduced by Archbutt,* in which the sample is heated in a stream of hydrogen with suitable precautions, and the oxygen is determined by loss of weight of the copper. Some analysts prefer to weigh the water produced by the reduction of the copper oxide. The "difference" method is simpler and quite satisfactory so long as there are no volatile impurities. The temperature required is only a low red heat. Oxide of zinc, on the other hand, is infusible and non-volatile in an oxidizing atmosphere at ordinary furnace temperatures. The temperature of reduction of ZnO is high, varying somewhat with the pressure and with the nature of the reducing agent. It is approximately 1000°C ., or, say, 50° to 100° above the boiling



·FIG. 1·

point of zinc. Hence any oxygen present as oxide of zinc cannot be directly estimated by loss of weight on heating in hydrogen, as a quantity of zinc would be volatilized when the oxide was reduced. Attempts have therefore been made to determine the oxygen in brass by means of the weight of water produced on heating the alloy in hydrogen. For this purpose a drying tube has been employed and weighed before and after the experiment.

As there was reason to believe that such a method was unsatisfactory, the reaction has recently been re-investigated in my laboratory by Mr. R. W. D. Nevill, B.Sc. The apparatus employed is shown in Fig. 1. It will be seen that hydrogen, which was obtained by the action of dilute hydrochloric acid

* L. Archbutt, *Analyst*, 1900, vol. xxv. p. 253; 1905, vol. xxx. p. 385.

on zinc, was purified by being passed successively through lead acetate, silver nitrate, and caustic soda. In order to remove any trace of oxygen the gas was then passed over heated copper gauze and through two drying tubes to absorb any water produced from the trace of oxygen. The hydrogen then passed through a hard glass combustion tube, the end of which was drawn out so as to avoid the use of a rubber bung connection with the drying tube and aspirator. The material to be tested is placed in a porcelain boat and is heated to redness with the aid of a small combustion furnace. The hydrogen, after passing through the combustion tube, was dried, and any increase of weight of the drying tube carefully noted. The second calcium chloride tube shown in the figure is a guard tube to prevent diffusion from the aspirator. The aspirator is furnished with a water manometer which is graduated in half-litres. By allowing water to enter through the tube from the water tap, or by drawing water through the bottom tube, the pressure in the aspirator can be normalized, and thus the quantity of gas passed can be read from the graduations. Blank experiments were first conducted in which hydrogen was passed through the apparatus so as to clean out any air, and then four litres of hydrogen were passed through the drying tube, which was always weighed when full of hydrogen.* The weight of the drying tube was found to be the same after the experiment as before, thus showing that the drying tubes were effective. In order to test the hydrogen for any trace of oxygen some copper strip was taken and was first heated in a glass tube in the hydrogen for about six hours to eliminate the whole of the oxygen originally present in the copper. A weighed drying tube was then inserted, and four litres of hydrogen were passed, after which the tube was removed and again weighed. As a result a regular increase of 0.0026 gram was recorded. This increase was apparently due to a small quantity of oxygen not removed by the copper gauze. A plug of platinized asbestos and a further length of copper gauze was then introduced, when it was found that four litres of gas only caused an increase in weight of 0.0002 gram in the drying tube, and this was considered satisfactory.

* Compare Greaves, *Journal of the Institute of Metals*, No. 1, 1912, vol. vii. p. 235.

Some brass turnings weighing 9.2203 grams were then substituted for the copper strip, being placed in a porcelain boat in the combustion tube. On expelling the residue of air and heating the brass turnings for ninety minutes in a slow stream of hydrogen, it was found that there was no increase of weight in the drying tube. There was, however, a ring of oxide of zinc formed at the edge of the zinc sublimate contained in the tube. These experiments showed that oxide of zinc might be in the metal in the heated portion of the combustion tube without any corresponding quantity of water being obtained. Experiments were next conducted with pure oxide of zinc, which was placed in the boat in the combustion tube, and heated to temperatures increasing up to 1000° C. It was found that there was no increase of weight of the drying tube, though a quantity of oxide of zinc was condensed on the sides of the combustion tube. The origin of this zinc oxide appears to be as follows:—

The hydrogen reduces zinc oxide to metallic zinc which volatilizes together with the water produced by the reaction. The water oxidizes the zinc vapour as the temperature falls and reproduces oxide of zinc and hydrogen, the nett result being that no water is carried away to be absorbed by the drying tube. This is in accordance with the observations of St. Claire Deville* and also of Dick.† The former observed that when zinc oxide was reduced by hydrogen, if the gaseous velocity was small, the zinc formed was nearly all reoxidized, but that with increased velocity of the hydrogen the proportion of metallic zinc obtained is greater. Mr. Nevill therefore proceeded to try experiments dealing with the effect of increased velocity of hydrogen, quantities up to one litre per minute being employed. Zinc oxide was heated in a porcelain boat to a high temperature as before. A considerable proportion of zinc oxide was reduced, and metallic zinc volatilized. The proportion of zinc was certainly much greater than with a slow stream of gas, but even with this excessively quick rate of passing the gas there was still a fringe of oxide on the sides of the tube.

* *Annales Chimie et Physique*, 1855, 3rd Series, 43, p. 479.

† Percy's "Metallurgy," 1861, p. 535.

It is, therefore, evident that no accurate determination of oxygen in brass can be made by adopting the methods which are suitable for copper. The volatilization of zinc from the sample when heated in hydrogen renders the loss of weight quite untrustworthy as an indication of the oxygen removed; while the secondary reaction whereby zinc vapour is oxidized by water vapour as they pass together out of the heated portion of the tube prevents more than a small proportion of any oxygen which is present from being absorbed as water by the drying tube. Methods of extraction of oxide of copper by digestion of brass turnings in ammonia are evidently quite untrustworthy, as there is reason to believe that copper oxide is not present in brass, and anything which is extracted is obtained merely as a result of errors in manipulation. A description of a simple and direct process for the accurate determination of oxygen in brass would be appreciated by many who are interested in the subject.

DISCUSSION.

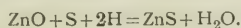
Dr. T. K. ROSE (London), in opening the discussion, said that he hoped the author would be able to solve the problems that he had mentioned in the course of the paper. He desired to ask the author whether the first reaction mentioned on page 249 could be expressed as a definite equation that could not be reversed in any way? Or whether, according to the temperature and perhaps other conditions, different mixtures were formed?

Mr. T. VAUGHAN HUGHES, Assoc.R.S.M. (Birmingham), said that every one who had been more or less identified with the brass industry had made an attempt to solve the problem of estimating oxygen in brass. Like the author, he candidly admitted that so far he had not succeeded in his endeavours. He had tried the hydrogen method some years ago. It would certainly be useful if any one could devise a method generally applicable to commercial brasses. With regard to the last equation chalked on the board, some years ago he made the following experiment, which he hoped would be considered *apropos*. Small strips of brass and copper sheet partly overlying one another were heated in a tube to about 700° C. Purified steam was passed over the test-pieces. Oxide of zinc was formed on the brass in parts not covered by the copper strip. On the other hand, where the copper strip covered the brass, zinc was deposited on the former, making a coating of brass at points of contact, whereas the copper remained quite bright where out of contact with the brass.

Mr. LEONARD ARCHBUTT (Member of Council) said he was very glad the author had brought the subject forward, because it had shown very clearly where they stood at present with regard to the matter. It was not a subject with which he had any practical acquaintance, as he did not remember having ever tried to determine oxygen in brass. If he had tried to do it he would probably have started as the author had done, by heating in hydrogen, and he supposed he would have ended by obtaining no result. It had occurred to him that it might be possible to take a weighed quantity of the brass, distil off from it in a high vacuum the zinc and all volatile matter; then cool down *in vacuo* and reweigh; then heat the residue of copper and oxide of zinc to a high temperature in hydrogen, and determine the loss of weight. Whether that would give a determination of the oxygen would depend on several things. First of all it would have to be proved that no oxygen was lost as a volatile oxide by heating *in vacuo*, which was not by any means certain. Another point was that on heating the residue afterwards in hydrogen to a red heat the loss of weight would not be oxygen but ZnO, because the zinc would go off as well, so that the loss of weight would represent directly the ZnO. He imagined that the quantity of oxygen in commercial brass that one would usually have to estimate would be so exceedingly small that such a method might not be practicable. In regard to that

he would like the author's opinion. It would not of course by any means answer his description of a simple method, but if a determination was required and they could not get it by a simple method, it was necessary to get it by a more complicated one. He thought it would perhaps be an advantage if the author would give some figures on page 252 showing what results actually were obtained by heating the zinc oxide in hydrogen, because it was not very clear at present whether a large proportion of the oxygen was obtained as water or whether only a comparatively small proportion was obtained. Mr. Tomlinson had just suggested to him that it might be possible by heating the brass in carbon monoxide to reduce the zinc oxide and weigh the oxygen as CO_2 .

Mr. G. A. BOEDDICKER (Member of Council) said that on looking at the second formula which the author had given it occurred to him that it might be possible to use Rose's well-known method of estimating zinc as sulphide by heating oxide or salts of zinc with sulphur in an atmosphere of hydrogen. Professor Turner's second formula would then read :



The best way would probably be to divide the estimation into two parts. During the first operation the deposit of ZnO would form on a part of the combustion tube. During the second operation the brass should be replaced by sulphur, hydrogen should be passed through the tube, the sulphur slightly heated to a gentle distillation, and that part of the tube containing the deposit of ZnO should be heated to 600° or $700^\circ \text{C}.$, at which temperature the above reaction would no doubt take place. Any excess of sulphur passed over should be retained in an asbestos filter.

Mr. F. JOHNSON, M.Sc. (Birmingham), said that a short time ago he carried out experiments in a similar way to those to which the author had referred, with exactly the same result. He thought it would be advisable if possible to seek for oxygen in brass by the aid of the microscope. The author stated that that was not possible; but it was stated in a paper* which was to be read later on at the meeting, and in an article by Greaves,† that zinc oxide was distinctly visible between the crystals of brass to which oxide had been added. Had the author since been able to identify zinc oxide by the aid of a microscope?

The PRESIDENT thought the members were very much indebted to the author for his paper. There was no doubt whatever that oxygen as it occurred in brass existed as zinc oxide. That could easily be demonstrated; when spelter is added to very dry copper, a brass is obtained that cannot be poured out of the crucible. So much zinc oxide is formed that the metal is perfectly pasty or may be solid. That proved distinctly, he thought, that where there was Cu_2O in copper and

* See Carnevali's paper, p. 282.

† *Chemical News*, Nov. 12, 1909, No. 2607, vol. 100, p. 233

zinc was added, zinc was oxidized and existed afterwards as oxide in the solid brass. With regard to the reactions, the makers of spelter had experience every day of the reaction between water vapour and zinc. When steam was present in the retort, part of the zinc which distilled over was almost at once oxidized. Mr. Archbutt had just suggested that by passing CO over the brass it might be possible to determine the amount of oxygen. Carbon dioxide was obtained, but carbon dioxide behaved similarly to steam. Immediately zinc vapour came in contact with carbon dioxide it was at once oxidized, so that reciprocal action took place also in that case.

Professor T. TURNER, in reply, said he was much obliged to those who had joined in the discussion on his paper. He was afraid when he wrote it that he had put too much detail into it, but two of the speakers had nevertheless asked for further figures. It was rather difficult to know what to do in giving a description in such a paper. With regard to Dr. Rose's inquiries, the exact nature of the action of oxide of copper and zinc could always be varied by varying the different proportions of the copper oxide. He had given the reaction in exactly the form in which he carried it out as being the simplest and most direct method, but it could easily be modified. So far as his experiments were concerned absolutely no weighable loss of zinc was obtained, when zinc oxide was heated with copper, although he heated to a temperature of about 1200° . He took it, therefore, that that reaction practically did not take place. He presumed that all such reactions went on to a very small extent—to the extent of a few electrons or something of that sort, but for practical purposes the reaction was perfectly definite in one way, and the converse did not take place. If he had an opportunity he would be glad to try Mr. Archbutt's suggestion of distilling over the zinc, and seeing if he could get the zinc oxide left behind. A similar method suggested by Mr. Law for other cases he thought would not work with ordinary metals with aluminium. The difficulty of volatilizing aluminium was too great; but, on the other hand, zinc could be volatilized from brass at a temperature of 1100° or 1200° so completely and easily that it was quite possible the reaction suggested might be better at all events than anything used at present.

Mr. LAW said the zinc oxide was volatile, too.

Professor TURNER said that oxide of zinc was perfectly non-volatile in an oxidizing atmosphere at a temperature of 1200° ; but if there was the slightest trace of a reducing agent present it would liberate zinc. Oxide of zinc was not volatile so long as there was no reducing agent present, and copper for that purpose was not a reducing agent. With reference to Mr. Johnson's question, he had seen enclosures in brass, and these were presumably zinc oxide; but one generally found there were little holes out of which the zinc oxide powder, or whatever might have been there, had fallen and been removed. But that something had been there they had every reason to believe.

On the motion of the President, a hearty vote of thanks was accorded to Professor Turner for his interesting paper.

COMMUNICATION.

Mr. H. J. YOUNG (Wallsend-on-Tyne) wrote that on page 250 the author stated "the 'difference' method is satisfactory so long as there are no volatile impurities." The writer agreed with this statement and held that it precluded the coppers and brasses of commerce, and condemned the method.

Professor Turner stated on page 252 that zinc oxide condensed on the side of the combustion tube without any increase in the weighing tube, explaining that by a reversible reaction, in which zinc oxide and hydrogen formed water and zinc, the two latter reacting together again to form zinc oxide and hydrogen. The writer believed that to be the case not only with zinc, but also with other minute impurities occurring in commercial coppers and brasses, and that was one reason why he personally had little faith in the method, particularly for purposes of research.

THE JOINING OF METALS.*

By ALEX. E. TUCKER, F.I.C. (BIRMINGHAM).

INTRODUCTION.

THE expression "The Joining of Metals" clearly includes such processes as riveting, folding, sewing, and dowelling. As these, however, are essentially mechanical processes I do not propose to discuss them. On the other hand, I shall be able to show that many industrial operations, such as riveting and folding, are now being replaced by autogenous welding and other recently introduced means.

Methods of joining metals by physical processes, such as welding and brazing, give rise to some interesting considerations, and it is the physical process involved in such operations and the commercial application of such operations which I propose to discuss.

The phenomena of cohesion and adhesion, on which the joining of similar or dissimilar metals depends, are frequently referred to as one and the same thing. It is therefore well to decide whether or not this interpretation is justified, and if it is not justified, to distinguish between them. It is true that in brazing copper and soldering together two pieces of brass other actions, such as alloying, come into play; but there are many cases on which I shall enlarge where cohesion or adhesion, or both, are depended on alone for the result, and lead to important industrial applications.

The etymology of the two words assists to some extent, but etymology is sometimes misleading, because current use and the authority of text-books frequently diminish its value. Perhaps I may illustrate the difference in the two phenomena of cohesion and adhesion as follows.

A sheet of paper may by well-known methods be divided into two sheets, the cohesion of the paper being thereby overcome; but unless the adhesion of the sheet of the material to the two surfaces of the material employed in the experiment is

* Read at Autumn General Meeting, London, September 26, 1912.

greater than the cohesion of the sheet itself, it cannot of course be so divided. Cohesion is therefore the tenacity of a material, and is functional and molecular. It is the tensile strength—in this case the transverse tensile strength—of the body. Adhesion is the external and adventitious property of media and conditions which resist the separations of the materials, and it may be less or greater than the cohesion or tensile strength of the bodies involved. In other words, the force which acts between adjacent parts of the same substance is called cohesion, while the force which acts between portions of different kinds of matter is called adhesion. Both forces are quite inoperative between two portions of matter separated by any distance which we can directly measure. Quincke examined the conditions of their operation and found that the greatest distance at which the effect of these forces is sensible for various substances is about the twenty thousandth part of a millimetre.

During unknown periods advantage has been taken of the phenomena of cohesion and adhesion in inlaying and buhl work, in which the strength of the joined work exceeds that of the material joined. Thus a design is drawn on two surfaces of wood—these designs need not be identical—and the design is then worked in with a thin glue, the other parts being damped and dusted with French chalk, to retard adhesion. After submitting the two pieces of wood—with an intervening layer of coloured wood—to pressure, and allowing the whole to dry, the intervening layer may be split into two lamina, after which the designs are brought out by cutting away the superfluous wood, followed by sand-papering and polishing.

I allude to this illustration of joining of wood and other materials, because, for reasons which I shall give, there is an application of the property of adhesion for the production of art metal work, though I do not know that it has ever been done commercially. I have only seen the results of experiments in this direction. In this case, however, the layer of metal is not split into lamina.

A more immediate example of cohesion may be given. In close annealing iron and steel sheets it sometimes happens

that two or more of the clean sheets, especially those at the bottom of the box, will stick together so completely that, instead of separating, a sheet will, if sufficient force be applied, part into lamina before the adhering media will be broken down.

The same thing happens in rolling many kinds of metal sheets when they are free from oxide—indeed, if oxide were present on the surfaces the action could not take place; on examining the points of contact it will be found that intercrystallization has taken place, and true welding has therefore occurred. Allied examples of this effect often occur in the seizing of shafts in their journals through failure of lubrication, or where a steel shaft has been allowed to revolve in or against a steel bearing or mass of similar quality. An interesting case is recorded in which the two ends of a broken shaft accidentally welded up again by the heat developed at the surfaces.

Generally, if surfaces of the same material are sufficiently parallel and polished, great adhesion may be obtained by simply laying them together. Plate-glass sometimes shows this effect so completely that the two may be cut and worked as a single piece. If the materials having such surfaces are ductile, and pressure is applied either by rolling or by simply dead weight, the effect is accentuated. I should regard such results as illustrations of cohesion rather than adhesion. These results have great practical value, to which I shall presently allude; but they seem to be only an extension of the undoubted cohesion effect, shown when two pieces of lead or phosphorus, or metallic powders, or mixtures of powders are compressed. Under the condition of pressure the effects are greatly accentuated by time and temperature, and true welding appears to occur.

The expression "welding" (A.S. *weallan*, to boil), in connection with non-ferrous metals, is borrowed from practice in iron and steel working, in which the pieces to be joined are brought to a high heat, often fusion heat, and are then hammered together. This operation is one which, from a physical point of view, illustrates the difficulty of saying whether the result is due to cohesion or adhesion. When high heats are used cohesion would appear to act, but it is

well known that fusion is not required for effecting a union of several metals to bring about a joint having a great degree of strength. Two clean pieces of any soft metal, such as lead, may be hammered or pressed together and a fairly strong joint made. Analysts often readily repair a perforated platinum crucible by cleaning the metal round the hole and hammering a piece of bright platinum while the two are at a red heat. The well-known Coffin's Weld is another instance; here the pieces of iron or mild steel are heated greatly below the fusion temperature in an ordinary reducing atmosphere and pressed together. The join shows remarkable strength, and Dr. Stead had recently shown that if the operation is modified, so that time is given to the period of contact, the crystals of the two surfaces interlock and the requirements of a true weld are obtained, the strength of the weld as a whole being determined by the degree of contact of the two original surfaces. Hence, by extending the time or raising the temperature, and maintaining a non-oxidizing atmosphere on the surface, an entirely satisfactory weld may be obtained at a temperature much below that ordinarily employed. These results illustrate in a practical way the conclusions arrived at by Quincke, to which I have already alluded.

Although there is a clear difference between the phenomena of cohesion and adhesion—and the difference is important when discussing the phenomena of joining of metals—it must be admitted that under certain conditions it is difficult to distinguish between the influence of the one and the action of the other; thus if two pieces of brass be joined by ordinary tinman's solder, it can be shown that a true alloying is obtained between the solder and the two surfaces. The strength at the surface of the pieces of brass will be the strength or adhesion of the alloy, but the strength of the work as a whole will be the strength of the intervening layer of solder. On the other hand, if instead of tinman's solder a material be used such as india-rubber, cement, or glue, or a film of oil or even water, the join will be effected by adhesion, as no molecular combination obtains between the brass and such media.

Although in the latter case the force required to separate the pieces of brass may be considerable, it appears to be

limited to the surface tension of the intervening layer. This is the explanation of the well-known fact that in cementing two surfaces by an intervening layer, provided the surfaces can be "wetted" by the material forming the layer, the thinner the layer used the stronger will be the adhesion. The join will also be more permanent, because it more completely adapts itself to the changes of temperature to which the whole may be exposed, whereas if a thick mass were used it might expand unequally with it, and possibly destroy the cohesion.

METHODS USED PRACTICALLY FOR JOINING METALS.

The methods in practical use for joining metals may be divided in the order of their importance as follows :

1. *By metallic cements*, such as tinman's or brazing solder, which have to be brought to the plastic or liquid state, and whose constituents should be capable of alloying perfectly with the metals to be joined.

2. *By autogenous fusing*, in which the two parts are heated and liquid metal of the same character run round the mass, or the parts are heated to fusing point, and the surfaces worked together by pressure or hammering.

3. *By the use of a cementing metal under pressure*, generally that of a rolling-mill, and at ordinary or only slightly raised temperatures.

In respect to the first method, it is obvious that the fusion point of the solder must be lower than that of the articles to be joined, and as, speaking generally, the higher the melting point the stronger the solder, it follows that it is desirable that such solder or brazing spelter should be used whenever possible, the melting point of which is only a few degrees less than that of the metals to be joined. The solder should also have, if possible, the same characteristics, such as malleability, colour, and hardness. This is especially important in jewellery work, and also in the brazing of copper. Such conditions imply greater skill on the part of the operator, but the union will be the more perfect, and the process under such conditions more nearly approaches autogenous soldering.

In the jewellery trade it is usual for the workman to make his own solder, because the colour and standard of purity, with respect to the contents of gold or silver, have to be very finely adjusted to the work in hand. The result is that, without any colouring of the finished work, it is often impossible to detect the join. It is hardly necessary to say that such results are only obtained by great experience. In joining such metals as britannia metal and pewter, both of which are alloys containing much lead, very fusible solders must be used: these generally contain bismuth, and the flux used is tallow or olive-oil, or its equivalent; further, instead of the flame of a blowpipe or a soldering iron being used, the workman will effect the join by directing a stream of hot air on to the parts, in this way greater control of heat being obtained.

Tinman's Solder.—In the use of this care should be especially taken to avoid the presence of zinc, and in certain cases even a trace of zinc is especially prejudicial; it thickens the solder, and probably on account of its liability to oxidation forms a superficial scum which the ordinary spirits of salt is incapable of dissolving. If the presence of zinc be suspected, the addition of a few drops of acid will help greatly. Antimony is frequently present in tinman's solder—this, by forming a cement of higher tensile strength, may, under special conditions, make a joint of greater strength. In the use of solder, either soft solder or brazing solder, it is clearly the correct method to raise the work to the highest temperature that the solder and the work will stand, because under such conditions the penetration of the solder into the surfaces to be joined will be better, and further, the soldering medium may then be squeezed out to the maximum from between the surfaces by suitable means, and hence the requirement can be met, that the thinner the layer of cementing material and the closer the surfaces are together, the stronger the join. Additional strength, because of the additional intimacy effected, may be given to the work by rubbing the surfaces carrying the liquid solder together; in the same way it is always well to rub the soldering iron, when possible, over the work when it is used, the “wetting”

of the surfaces is then more perfect, and no stripping of the solder is possible when this rubbing is done. In order to obtain a lower melting point in tin solder, bismuth, and sometimes cadmium, is added. Such solders are used for delicate work, as is occasionally required for electrical fittings.

I am aware of bicycles having been built in which the tubing was fixed in the respective lugs with soft solder instead of the ordinary brazing. They stood every test, and personally, if the lugs are carefully machined to only a fraction larger than the tubes, I should prefer this method of frame building.

The conditions here are very different from those in the case of the brazing of brass and copper, because it happens that all the metals employed in brazing and tinman's solders destroy the character of the steel they are intended to join if they are heated sufficiently with the steel, while they have no corresponding injurious effect when used for brass or copper work.

When soft solder is used the thin gauge tubing is not so likely to be spoiled by deteriorating action on the steel, or by being oxidized at the heat necessary for brazing; and, further, on account of the greater liquidity of the soft solder, it will, when properly applied, sink into the small annular space between the lugs, &c., and the tubes more completely than can be expected with the more viscous flux and brazing solder. The reasons that soft solder is not used for such work are, firstly, because the heat of the enamelling stoves makes its use risky; and secondly, popular prejudice—a soft soldered frame sounding badly to the untechnical layman.

It is a common habit of workmen, and amateurs who have soft soldering to do, to depend on the ordinary bit, when they might use a bunsen or blowpipe. These, in many cases, would heat the work more generally than is possible with the bit, and would allow of the penetration of the solder into the surfaces, and the subsequent squeezing out of the excess of solder.

On the other hand, many forms of soldering bits are now in use, in which a bunsen-burner connected with a light flexible tube is employed to heat the bit, and the flame can be

conveniently made to heat the work as well. This form of soldering iron has many advantages. One of the best fluxes I have found for ordinary soldering can be easily made by macerating flux skimmings from galvanizing pots with weak hydrochloric acid. On filtering, the solution is ready for use, and is an ideal flux, because of the chloride of ammonia present with the chloride of zinc. No iron or lead is dissolved if the acid added is not in excess. Solder is often used in the form of granules or strips of various sizes, and in this form is very convenient for routine work. In the case of spectacle frames or other light articles a large amount of work can be prepared, on each of which a small piece of solder, either in the form of a granule or a strip, is placed with flux on the part to be joined. The articles are then put in a tray, which is afterwards taken to a muffle working at a convenient heat, or in some cases it is sufficient to put the work on a metal plate, heated by a gas flame or even a spirit-lamp. Brass tubes are often made by bending the strip through dies, and fixing a wire of suitable composition in the overlap with borax, or the borax may be mixed with finely granulated spelter. On passing the work through a furnace to raise it to a red heat, the spelter runs perfectly and a good join is made. The flux is then dissolved off the work, and the tubes are finished by drawing through dies with or without a mandrel.

The best brazing, if it may be properly so termed, is done with "silver solder," thus the blading used in turbines is all fixed with silver solder. It is of course of the utmost importance that the small pieces used in the construction of turbine motors shall be immovably fixed and cemented in position, on account of the heat and centrifugal strain to which they are subjected. Various silver alloys are used, but they are generally about 60 of silver, 23 of copper, and 17 of zinc, the flux used being borax, or borax and carbonate of soda. Such a mixture is remarkably liquid when in the molten state, and on this account penetrates interstices which ordinary brazing spelter would fail to fill.

Brazing Solder.—The composition of ordinary brazing solder ranges within wide limits; the analyses of samples I have

examined show a variation from 61 to 33 of copper, and 39 to 67 of zinc. The tin may vary from nil to 14 per cent., and the lead from nil to as much as 3 per cent. Any of such metals may be and are used for brazing, in accordance with the character and requirements of the work to be done. The higher the percentage of copper the higher the melting point, and the higher the percentage of tin the lighter the colour. We thus have a very large series of alloys available for very varied requirements. The presence of other metals when in small amounts is often of no consequence in the brazing of brass or copper, though obviously in all cases it is very desirable in important work, such as the brazing of high-pressure steam-pipes or where great strength is required, that the composition of the brazing metal shall approach as closely as possible to that of the metal to be joined, as only under such conditions can the maximum strength of the joint be obtained, and it is the non-observance of these conditions which has led to disaster. The skill of the workman is often limited to the fluxing of the solder, and seldom extends to an appreciation of its composition.

When, however, we come to brazing iron and steel the importance of purity is very much greater, and I have found the presence of tin in brazing solder intended for bicycle frames to be very injurious. The explanation is probably to be found in the extraordinary deleterious effect of tin on iron and steel. It is well known that a very small amount of tin scrap, if allowed to get into a bath of molten steel, will make it very red short, and when brazing solder containing as little as 0.5 per cent. of tin is used for brazing bicycle frames, I have found that the joints are very unsatisfactory and unsafe.

An ingenious method of making a brazed joint is by connecting the two parts to be joined with the terminals of a suitable dynamo. On account of the local resistance the two parts become heated, and if suitable brass wire is wrapped round the tube, in the case of a cycle frame, and the whole surrounded with a reducing gas, such as hydrogen or coal gas, a very perfect joint is obtained without any borax or other fluxing medium.

The reducing gas under such conditions will ensure the absence of any oxide of iron or other metal used, and no previous cleaning is required. Such methods of joining has the great advantage that there is no borax to remove from the joint. On account of its great hardness this removal of borax is a serious matter, and much money has been spent on experiments to remove it by pickling, and other methods. It is best removed by sand-blasting, the whole frame being so treated leaving an excellent surface, on account of its roughness, for enamelling.

Liquid Brazing.—Several patents have been taken out for details of apparatus in which a bath of brazing spelter has been kept liquid. The parts to be joined are dipped in the molten metal, the metal being prevented from adhering to the parts that have not to be brazed by applying a coating of blacking to them. The advantage of this method consists in the fact that less metal is used in making the joint, as so little is lost in applying it, and also the heat is general on the joint instead of being local, and I have no doubt that on routine work the consumption of gas for heating is less than when blowpipes are used, and of course blast is not required.

A modification of brazing is the use of copper in the form of sheet or wire. Under the Simpson patents tools are thus made in which the cutting part is a small piece of high-speed or other steel, while the shank is mild steel or iron. In making, say, a lathe tool by this process, a bar of square mild steel is taken, and a channel planed or milled out on it in which a suitable square piece of high-speed steel fits. The two or three sides being clean, strips of copper are fitted in with a special flux, and the whole highly heated to the fusing point of the copper. After welding, the compound tool is cleaned up and treated for hardening and tempering in the ordinary way. There are some features about this process of building up tools which seem to have considerable merit. First, if ordinary brazing were used, the hardening of many tools implies such a temperature as would often destroy an ordinary brazed point. The zinc would possibly be volatilized, which is not the case when copper alone is used, the temperature of fusion of the copper being so much higher. Secondly,

it is conceivable that the weld would be considerably stronger than with an alloy of zinc, because while copper alloys to a considerable extent with iron, the same cannot be said of zinc, which therefore under such circumstances would become a deteriorating element. Thirdly, the saving of expensive material, such as alloy steel, must be considerable in the case of heavy machine tools, as only a small portion of metal is ever in actual use. In a sense, therefore, the shank becomes a tool-holder without the disadvantages of the latter in respect to unsteadiness, difficulty of setting, &c. The process lends itself to many interesting applications; thus milling cutters may be made having a core of mild steel instead of tool steel. Hardening and tempering such cutters is a source of much difficulty and loss through distortion and cracking, and if the compound cutters can be so produced the possible economy should be considerable. There is no doubt as to the perfection of the join, as I have seen pieces of steel joined by the process which on splitting did not part at the weld, the original metal appearing to be the weaker material.

THE BRAZING OF CAST IRON.

A process has been invented by F. Pich (Berlin) for the hard brazing of cast iron in a smith's hearth. The patent consists in the decarburization during brazing of the cast iron surfaces to be united, and in bringing at the same time the molten brass solder into close contact with the cast iron surfaces which are decarburized, but without exposure to the air. For the decarburization of the surfaces copper oxide is used, which is mixed with borax, as a flux, until it has the consistency of a paste. This is applied to the surfaces to be joined, which must first be carefully cleaned. The cast iron pieces are then firmly tied together with wire and heated. The borax first melts, protecting the surfaces from oxidation, and taking up any oxide that may be still clinging to them. It also precludes the attacking of the copper oxide by the oxygen of the air. As the heating proceeds the copper oxide fuses and gives up to the now red-hot surfaces its oxygen, which combines with the graphite of the cast iron forming

carbon monoxide and dioxide, while the metallic copper is set free in a very finely divided state. This alloys with the brass solder as it melts when strewn on, and the new alloy combines with the decarburized iron of the surfaces which it is desired to join.

Specimens of cast iron united by this method were prepared and subjected to tensile and breaking tests, and the summary of all the results shows that when the brazing of cast iron pieces is carefully performed according to the details given by Pich, the strength of the pieces so joined is virtually equal to that of the solid material.

THE SOLDERING OF ALUMINIUM.

As is well known numerous patents have been taken out, and numerous mysterious mixtures have been advertised for the so-called soldering of aluminium. In nearly every case the result is that, while fairly satisfactory for a short time, the join failed after a time, varying from a few days to some months. One of the most severe tests to which such joins in aluminium can be subjected is that of warm steam. Joins which look well and are apparently mechanically strong, fail rapidly when submitted to this test. In all soldering, it is obvious that the flux used must efficiently clean the surfaces of the metals to be joined, otherwise no alloying of the solder used with the surfaces is possible. In the case of aluminium very few materials adapted for such fluxes are available, the requirement being that they shall absorb oxide of aluminium. Another detail of importance is the great heat conducting of the metal. A consideration of the results obtained with all the so-called solders of aluminium shows that the metal is so susceptible to electrical action and oxidation that the use of any metal in which aluminium itself does not preponderate is hopeless. The best results have invariably been obtained when the solder was of the same composition as the material to be joined. This condition involves the principle of autogenous soldering, which will be subsequently dealt with. The best flux used is a mixture of alkaline aluminium chloride, with the addition of fluorides, such as potassium fluoride or calcium

fluoride. When these are mixed in suitable proportions and damped with alcohol, and heated on a strip of aluminium, the surface of the metal is cleaned perfectly. It therefore follows that if two surfaces of aluminium are so cleaned, and an alloy containing a high percentage of aluminium, with such addition of other melted metal as will reduce its melting point slightly below that of pure aluminium, applied with the flux named, that a very satisfactory join will be obtained. The heat such as from a spirit-lamp or bunsen-burner must, however, be applied from below the work. I have seen such joins made over a spirit-lamp which stood every test, including that of the steam test.

Difficulties arise from the presence of high percentages of aluminium in alloys in connection with soft soldering. These may be largely overcome by coating them electrically with copper. The following directions for soft soldering their alloys, containing from 5 to 10 per cent. of aluminium, have been issued by an electric smelting company:

"Cleanse well from dirt and grease. Then place the part to be soldered in a strong solution of sulphate of copper, and place in the bath a rod of soft iron, touching the parts to be joined. After a while a copper-like surface will be seen on the metal, remove from the bath, rinse quite clean, and brighten the surfaces. The surfaces can then be tinned in the ordinary way."

It is obvious that these directions are intended to be used only where an ordinary electrotyping plant is not available.

AUTOGENOUS FUSION.

The second method of joining metals referred to is that of autogenous fusion or running liquid metal of similar character on to the surfaces to be joined, and in its simplest form is very old. It is illustrated in the case of repairing broken rolls and in lead-burning. It has been a practice for the broken surfaces of rolls to be cut away to give room for the new metal. The whole roll is then heated, and hottest possible metal run into the intervening space, with suitable headers to allow of escaping gases. I have seen very successful jobs

made under these circumstances, and the system is obviously applicable to many other cases.

In the wiping of lead joints for water services we have an example of semi-fusion welding, for, as is well known, the metal used, invariably a mixture containing a high percentage of tin (lead 33, and tin 67), is always in the plastic state during the operation. Great skill is shown by the workman who frequently makes his own metal, not only in so adjusting the addition of the tin that he can tell by its appearance whether he is right or wrong, but also in his use of it, because the heat at which he applies it has to be adapted to the work in hand, and judgment must be further exercised in seeing that the successive layers he applies are really melted or crystallized on to the preceding chilled ones without any "cold shutting." This process of wiping a joint looks very simple, but undoubtedly it requires a great deal of experience and observation for its successful practice, and many branches of plumbing in which the various pieces of lead are joined show a very high order of technical and manipulative skill. On the other hand, I am told by good practical men, that if they had their choice there are many cases where they would not wipe the joints. Thus, if a union or cock has to be fixed in a lead pipe, the pipe can be coned or socketed and tinned inside, and if the union or cock to be fixed is also tinned and driven in the pipe, and tinman's solder with extra tin be melted in the annular space with a soldering-iron and finished with a blowpipe, a perfectly satisfactory join results. I think that this is so is obvious, as the bursting strength is clearly greater at such a point than that of the pipe itself. It is also obvious that the bursting strength of most of the wiped joints is unnecessarily greater than that of the pipe on which they are made, and so expensive metal is correspondingly wasted. Two ends of lead pipe may be joined perfectly by fitting one into the other and tinning both surfaces and using solder, as above mentioned. Such joints, however, are not recognized in England by public authorities, though I have often seen them, with variations of detail, on the Continent. Thus I have seen a tinned brass tube inserted in the two ends and the whole soldered up—this makes a very neat and cheap joint.

The application of autogenous welding by acetylene, hydrogen, benzol, petrol, or other hydrocarbon vapour to commercial purposes has extended enormously during the past few years, and constructions and work are now possible by the use of such methods, which could not be carried out by any other means; thus repair work of ferrous and non-ferrous metals is now done in every town of importance, and tubes of all sizes are made on a very large scale. For branch pipe construction the process is quite unrivalled. For high-pressure steam-pipes the joints after screwing are often welded up, and metal vessels instead of being made with folded joints are now made with the blowpipe more cheaply and far more efficiently. Lead-burning forms an excellent practice for acetylene welding, as it is fusion welding in the simplest form. It is usually carried out with hydrogen and air, and if the workman can make a good joint with and without a stick of lead, it is a very easy step for him to advance to making one of aluminium or steel, or any metal. Lead burning, which at that time seems to have been also known as "autogenous soldering," was first introduced about 1833 by Mr. Mallet, although the invention was also claimed by Professor Daniel of King's College, and Mr. Thomas Spencer of Liverpool read a paper "On the Theory and Practice of Soldering Metals," before the Liverpool Polytechnic Society in 1840, in which he also claimed the discovery of the process. The advantages of such soldering were at once appreciated, especially for chemical works. The objections to ordinary tinman's solder were the great local action set up by varied metals used; and further, the contraction and expansion of the solder under the influence of heat is different to that of the lead which it joins, and so leaks are much more likely to develop.

Fletcher of Warrington was the first to introduce autogenous welding. This was in 1888, but he had no commercial success, partly on account of the low heating power of the oxygen and coal-gas which he employed, and, secondly, on account of the poor quality of the oxygen at his disposal. Further, the blowpipe used was very imperfect; there was great difficulty in maintaining a uniformly reducing flame. The first practical success with fusion welding was obtained

by the late Felix Jottrand of the Oxyhydric Company of Brussels, who also introduced the first commercially successful application of oxygen for the opposite purpose, namely, the cutting of iron with oxygen, a process also previously demonstrated by Fletcher.

Jottrand's success was undoubtedly due to the fact that the gas employed by him was made by the electrolysis of water, and so was of high quality, and his blowpipe, though complicated, was very efficient. It is still a disputed point whether under some conditions his method with oxy-hydrogen is not better than oxy-acetylene. In either case it is important that the oxygen used be considerably less than the theoretical amount required, in order that although only a lower flame temperature is available the flame will always be reducing in character. Benzol, petrol, and other hydrocarbons have been recently used in place of hydrogen and acetylene for autogenous welding, and their use would under certain conditions have advantages.

THE OXY-ACETYLENE PROCESS.

In practice I have found that a proportion of four volumes of acetylene to five of oxygen gives much better results than the theoretical two volumes of acetylene to five of oxygen. So important is this detail that blowpipes are now generally constructed to consistently maintain a reducing flame. Such a blowpipe is that of the Drager-Greishiem. In this blowpipe the automatic reducing valves on the cylinders are fitted with gauges, which instead of being graduated to pressure are marked with the thickness of the material to be welded—all, therefore, that is necessary is for the workman to adjust the springs on both regulators, so that both gases indicate the same thickness. A simple mechanical mixture is arranged on the blowpipe, making the whole apparatus very practical and convenient.

A characteristic of the oxy-acetylene flame is that it indicates the correct mixture, for when the acetylene is in excess a small green cap appears over the inner cone of the flame. On reducing the oxygen there is a point at which the cap dis-

appears. The right mixture is just at this point, and the effect is so distinct that when working with acetylene the workman has no excuse for not getting the right proportion.

If temperature were the only consideration, the oxy-acetylene process would be used in all cases in the working of thin metal, but its use requires much greater skill than the lower heat of the oxy-hydrogen flame. Then again, when a fixed acetylene generator is not available, the risk and danger of a portable generator is considerable, and in such cases for oxy-acetylene welding "dissolved" acetylene only should be used. On the other hand, this is very expensive, and the apparatus is heavy, and it therefore follows that the oxy-hydrogen method with its complete portability is very often to be preferred, because hydrogen can be obtained in the usual bottles, and thus forms very convenient plant.

In welding metals other than iron, not only the melting point but the heat conductivity of the metal must be considered. Thus copper with its high conductivity and its low melting point can hardly be worked with the oxy-hydrogen flame. Indeed, for the same section as iron it requires a much more powerful oxy-acetylene flame. Brass, bronze, and indeed any metal, may be autogenously welded, and many require much less care than that for aluminium.

The conditions of success which apply to all welding with acetylene or other hydrocarbons are—(1) the use of pure gases; (2) the use of a metal rod of approximately the same composition as that of the work to be joined; (3) the thorough fusion of the inside surfaces before the additional metal is applied; (4) cleanliness of the parts, and when desirable the use of suitable deoxidizing and fluxing powders, such as charcoal and borax, and lastly, the use of a blowpipe capable of complete control in respect to size of flame and proportion of mixture. With extended experience in the autogenous joining of non-ferrous metals, it is to be expected that this method will replace ordinary brazing where quality of work is of the first importance.

It should be noticed that in consequence of the highly local heating action of acetylene, contraction strains are likely to be set up, which may be more serious than those occasioned when

the whole work is heated and welded up in the smith's fire in the ordinary way. In the case of cast iron, it is very desirable that such strains should be avoided by making the weld first and then reheating the mass as much as possible, and cooling slowly. With respect to steel, it has been repeatedly shown that an acetylene or electric weld should not be hammered while the weld is being made. It is well known that cracks are likely to be made by hammering the metal at a black heat, a temperature occurring quite close to the point of fusion. The work, therefore, should be allowed to cool slowly and then raised to a high temperature in the ordinary way and not by the blowpipe; the weld can in this way be much improved both in shape and strength. A good fusion weld very seldom breaks at the point of welding—indicating, therefore, that this point is stronger than the neighbouring metal. I believe this is the explanation of the paradoxical effect noticed with fusion welding, that thick sections never give as high a tensile strength as thin. I have figures showing this.

Thus $\frac{1}{16}$ inch 3 per cent. nickel steel strips gave 97 per cent. strength, $\frac{1}{4}$ inch gave 90 per cent., while 1-inch bars broke at 60 per cent. to 70 per cent., with the fracture clear of the weld every time. Again, welded $\frac{1}{2}$ inch copper rods drawn down to $\frac{3}{8}$ inch in the ordinary way gave regularly 95 to 97 per cent. as compared with the original drawn rod.

THE USE OF ALUMINIUM POWDER.

There is an interesting series of processes for the auto-genous joining of metals, most of which are patented, which depend on the reducing power of aluminium. Any one who has seen the application of the Goldschmit or Thermit process to the joining of the ends of tram-rails can hardly fail to be struck by its extreme beauty and simplicity. We have here a small steel foundry not much larger than a silk hat, from which the metal pours in a perfectly liquid state.

As showing the great heat obtainable when aluminium powder is used for welding, it may be mentioned that if a wrought iron plate 1 inch thick is placed under the crucible, the liquid metal when tapped will burn a hole straight

through it, leaving a fairly smooth edge. Experiments show that the heat of the molten metal approaches 3000°C ., the temperature of a Siemens furnace being about 1600°C .

This Thermit process has been applied for the repair of ship's sternposts and other large fractures, and means have been adopted for heating up the fractured surfaces to the proper temperature before pouring in the cementing iron without damaging the clean metallic surfaces. This is done by building up the moulding-box around the fracture in such a way that it may act as a flue or chimney to an outside fire worked with a compressed air-blast, which dries the sand mould and heats up the metal very rapidly. The presence of even a small trace of moisture in the mould gives rise to blowholes in the thermit iron, hence great care must be taken that the mould is as dry as possible. The repair of the sternpost of the German Lloyd steamer *Friedrich der Grosse* was effected in this way. The only doubtful point in the process is the possible formation of internal fractures or cracks, but it is stated that in all the tests of the results fracture has invariably taken place outside the welding region.

It is very probable that in point of strength most thermit welds are superior to those electrically made, because the volume of heat is greater if not more intense, and, again, there is less risk of the original surfaces being burnt or oxidized. The thermit metal can also be adjusted to carry reducing media, which would quite eliminate any oxidizing influences.

Thermit proved useful during the Russo-Japanese War, especially on the Russian side. After the first attack of the Japanese on the Russian fleet at Port Arthur several tons of thermit were forwarded to the Russian Government, and the speedy repairs of many of the Russian ships were due to its use.

ARC WELDING AND RESISTANCE WELDING.

A third system of autogenous welding is the electric, of which two methods are in use—namely, arc welding and resistance welding.

Arc welding is applied for repairing breakages and filling

up flaws in castings, while resistance welding is rapidly being adopted for the working up of metal articles, and it is common to find electric plant in operation for sheet-iron working. Two forms of machines are on the market for this purpose, one known as the Spot-welding Machine, and another for Butt-welding. In the spot-welding machine the sheets are joined at spots instead of rivets, hence the name. The electrodes are shaped in accordance with the work to be done, and are put on to the work by pressure effected by a foot-lever, and the current, which is automatically switched on at low potential, welds the parts together at that point. After removing the foot-lever the work can be moved along for welding at a new point.

The entire process is so rapid that an unskilled workman is able to make 1000 welds per hour on plain sheets, while in the same time an experienced hand could hardly put together a quarter as many rivets. The up-and-down movement of the upper electrode may be performed automatically by means of a motor electrically worked. The electrode then falls and rises at regular adjustable intervals, and the workman only has to move the pieces of work.

This machine may also be applied on water-tight welding. In this case the travel of the work takes place slowly, so that the points of welding lie close together, forming an unbroken seam. The edges of the sheets are completely softened, and are pressed together seamlessly. Similarly, when the sheets are not too thick, and irregular shaped sections do not have to be dealt with, the spot-welding machine makes a very satisfactory weld. Thus wheel rims for cycles and motor-cars can be joined perfectly by its means, while the advantage of this system for welding handles on covers, or for welding rings on cooking utensils, &c., are conspicuous. In the same way half-stampings, such as kettle spouts, make up to a very satisfactory job with seamless welding.

Spot-welding is coming into very extensive use for the manufacture of kettles, buckets, and similar articles in which the surface is required to be joined only in parts.

In the case of kettles intended for enamelling the old form of riveting occasioned difficulties when the goods were

enamelled, because the edges of the rivets and the edges of the sheet refused to take the enamel, or in such thin layers as to interfere with the appearance of the finished work. The difficulty has been avoided and riveting rendered unnecessary by fusing the parts which were formerly riveted by means of the electric arc. The two surfaces are fused together at the point at which the arc is applied, and the enamel can then be run on without any difficulty.

Again, in the manufacture of gas-stoves, where it is desirous to have a layer of air between two sheets in order to economise heat, spaced depressions are made by means of a blunt punch on the sheets, and the sheets put back to back. On applying the arc to the depressions the apices of the latter are fused together, after which the sheet or sheets are enamelled in the ordinary way.

The same process is applied to other goods in order to avoid riveting, and one other advantage is the one of greater permanency in point of mechanical strength, where the goods are alternately heated and cooled. Under this condition of heating and cooling, rivets were often becoming loose, and so occasioned trouble. Galvanized work can be spot-welded. The zinc volatilizes off, leaving the iron exposed at the point where the dies come in contact with the metal.

The acting electrodes can be made into various shapes to suit special work. Thus, one can be made circular, freely movable on its axis, while the upper one may be formed of a circular piece of copper swung by a lever. Such electrodes are useful for welding short seams, such as triangular spouts of coffee-pots, &c. As the pressure put upon the material is very high, it will be understood that there is hardly any difference in strength between the welded and the unwelded material.

COMPOUND SHEETS.

The manufacture of compound sheets of metal is very old; thus, years ago, capsules for bottles containing liquids intended for domestic purposes were made from a compound sheet of tin and lead. The tin was used to prevent any action of such liquids on the lead—lead being a cheap and ductile metal which

could be easily folded over the vessel, and so made water-tight. Such compound sheets were made by passing a sheet of lead and of tin together through hot rolls, when complete union of the two was effected. Another illustration of compound metals is that of French plating—articles such as steel blades or knives, or flat brass surfaces, were plated by placing a sheet of silver on each side of the article to be treated. The whole was then bound with wire and heated in a muffle or other suitable furnace until a union at points was effected, after which the surfaces were burnished to improve the union, the whole being kept hot. Such goods were not, however, very permanent, and in the case of iron and steel work this might be expected, on account of oxidation. In Sheffield plate, which is also made in Birmingham, such plating is done exclusively on copper or its alloys. An ingot of such metal free from defects is well cleaned and coated with a saturated solution of borax. A sheet of silver is then laid on one or both sides of the ingot, according to whether the work is for single or double plating. The amount of silver used is considerable—thus for single plating it varies from $\frac{1}{24}$ to $\frac{1}{30}$ of the total weight, while for double plating this proportion is preserved in the double plating—*i.e.* the sheets of silver are half the gauge. After adapting the silver, the surfaces are brushed over with a saturated solution of borax, and the work bound together with wire. It is then heated in a furnace till the borax begins to run. The heat is carefully watched to prevent the silver running completely into the ingot. The point at which the work should be drawn is that at which the silver is drawn down flat on the surface. The operation is complete when a layer of solder is formed between the silver and copper, hence the care required in watching the heat. After removal from the furnace the work may be rolled to any desired thickness if properly annealed between the passes. After annealing, the metal may be treated as a homogeneous material, and may be raised, spun, stamped, or otherwise worked. Tubes or wire of Sheffield plate are produced as follows. A strip of silver is formed into a rough tube with an overlap; a red-hot copper mandrel is then inserted into this, and the overlapping edges of the silver are made to adhere by hammering and burnishing. This tube is

then cleaned inside, and a sliding fit made of it over a copper rod covered with borax; the ends of this rod are roughly grooved in order to engage the sheet of silver better, and also to exclude the air. The whole is then heated to redness and burnished down, after which it is passed through dies or beading machines, as required.

The last system of joining metals to which I desire to direct attention is the one in which the surfaces are not melted, but only slightly heated.

During recent years the manufacture of compound metals, such as nickel and steel, copper and steel, aluminium and copper, has become of great practical importance, and many beautiful articles are now sold for domestic purposes. The nickel steel, copper steel, or nickered zinc sheets may be obviously produced electrolytically, and afterwards rolled down to gauge, allowance being of course made for the ductility of the softer metal. But another method has lately been introduced in which sheets of different metals may be joined perfectly.

The manufacture of aluminium copper sheets illustrates the process, and further is interesting from a metallurgical standpoint. One method with which I am familiar is as follows. The copper sheet is pickled and cleaned. Aluminium powder is then brushed on by machinery, or by rubbing the surfaces with brushes or rollers of aluminium wire. A sheet of cleaned aluminium is then placed on such a surface, the two are heated and passed through rolls. The union is perfect, and hence the compound sheet may be subjected to stamping, spinning, &c., without any trace of lamination.

In the same way copper and steel, or almost any two or any number of sheets of different metals, may be compounded. The aluminium acts as a metallic adhesive. While rolling such sheets the top surfaces are often kept oiled to retard oxidation, and to obtain better finish.

In view of these results, it would appear probable that the method could be modified in such a way as to produce ornamental designs by similar methods as those employed in the inlaying of wood already described, with the difference that two sheets would be employed and not three, on account of

the impossibility of splitting the ornamental sheet, as is done with wood. Further, although I have not seen it done, it becomes possible by slight modification of the process to produce a design having several differently coloured metals, thus giving effects similar to those produced by parcel gilding or plating.

A second method of making a compound sheet of different metals is that in which an oxide or sulphide of a metal which will alloy with both of the two sheets is taken and mixed with aluminium powder, and the mixture laid evenly between them. The whole is then heated to the fluxing point of the mixture and then rolled, and as the two sheets to be joined receive the full heat of the furnace in which the work is placed, it will be understood that the alloying of the metal from the mixture with the two surfaces of the sheets is very complete.

In another method, where still more heat is used, for the production of compound plate, say, of aluminium and copper, copper or other wire gauze is placed between the sheets, and the interstices filled as before with aluminium powder and flux, consisting of alkaline chloride, and fluoride.

On heating the whole and rolling, the surfaces unite as before described, and probably more perfectly, because the gauze retains the flux better during the heating, and so does its work better, and is afterwards squeezed out by the rolls, while in addition there would also be the knitting or dowelling action of the gauze during rolling, which would further tend to hold the sheets together.

The use of such wire gauze would seem to be applicable to certain conditions of brazing, especially when the greatest care is necessary to produce the highest quality of work, such, for instance, as the brazing of steam-pipes to which allusion has already been made.

AUTOGENOUS WELDING BY MEANS OF OXYGEN AND ACETYLENE OF COPPER AND ITS PRIN- CIPAL ALLOYS, AND OF ALUMINIUM.*

BY DR. F. CARNEVALI (ROYAL POLYTECHNIC SCHOOL, TURIN).

INTRODUCTION.

IN a previous paper, presented to the October 1911 Meeting of the Iron and Steel Institute,† dealing with a series of investigations concerning the oxy-acetylene autogenous welding of iron and steel, I pointed out that the enormous development which this process has undergone within the last decade in regard to wrought iron, steel, and cast iron, has led to its extension to other metals of common use, such as copper with its chief alloys and aluminium. The empirical manner, however, in which the process has been applied in this new field, and the lack of systematic and complete researches, have conduced to results so diverse, often imaginary and discordant, as to permit of the formation of contradictory opinions, and thereby to arrest its possible further development. With the view of eliminating these uncertainties and contradictions in regard to the new process, and with the view also of increasing the knowledge thereof and of obtaining data of practical utility, I have undertaken, as complementary to the series of investigations carried out on iron and steel, the study of the oxy-acetylene welding of various metals (iron excepted) largely used in modern industry, particularly copper and its principal alloys, and aluminium. As stated in my previous paper, the literature of the subject is practically non-existent, such publications as are known generally taking the form of a disguised advertisement of a particular process or a particular firm, and are conspicuously lacking in complete and precise data. I may simply mention an article by L. Springer,‡ where good results are said to have been obtained

* Read at Autumn General Meeting, London, September 26, 1912.

† "Autogenous Welding of Metals," *Journal of the Iron and Steel Institute*, No. 11, 1911, vol. lxxxiv. pp. 188 *et seq.*; see also *Metallurgia Italiana*, October 1911.

‡ *The Foundry*, vol. xxxv., 1909.

in the autogenous welding of bronze and aluminium castings, but without the confirmation and the guidance which are the corollaries of assiduous investigations. On the other hand, the data supplied in a recent paper by R. Baumann,* in regard to certain researches carried out on the autogenous welding of sheets of aluminium, although interesting in themselves, are too incomplete and restricted.

The investigations which I have conducted were planned on the same method as those already published in regard to iron and steel,† and were subject to analogous criteria. I have endeavoured to comply with all the conditions essential for obtaining favourable results, and to overcome as far as might be the difficulties which most frequently attend the autogenous welding of metals.‡ At the same time, I have tried to reproduce as closely as possible the conditions which can be obtained in practice. It would seem, therefore, unnecessary to repeat in this paper what I have already written on these points, and it will suffice to refer the reader to the publications previously quoted, wherein I have given full details of the methods followed throughout the various series of experiments.

I propose to divide this group of researches on the oxy-acetylene autogenous welding of metals largely used in practice, other than iron, into two groups, as follows:—

First Group: Oxy-acetylene autogenous welding of copper and its principal alloys.

Second Group: Oxy-acetylene autogenous welding of aluminium.

FIRST GROUP.

OXY-ACETYLENE AUTOGENOUS WELDING OF COPPER AND ITS PRINCIPAL ALLOYS.

1. Copper.

A first series of experiments was carried out with pure copper, containing 99·9 per cent. of the metal, the metal used

* *Zeitschrift des Vereines Deutscher Ingenieure*, vol. lv., No. 2016, 1911.

† *Journal of the Iron and Steel Institute*, No. II. 1911, vol. lxxxiv. pp. 188 *et seq.*

‡ Compare in this respect my paper on "Autogenous Welding of Boiler Plates," *Rendiconti dell' Associazione Italiana fra Utenti Caldaie a Vapore*, September 1911.

for the weld being copper wire of equal purity, supplemented in certain cases by a small quantity of phosphorus, in order to obviate possible oxidation of the metal during the process of welding.

The samples were cut off round wire-drawn rods, measuring 35 millimetres ($1\frac{2}{5}$ inch) in diameter: each sample was sawn half through, and the edges were thrust apart in the form of a V at an angle of about 45° . After welding, some of the samples were cooled in air, while others were subjected to various thermic and dynamic processes; and, being thus prepared for mechanical experimentation, were so treated as to undergo a notable diminution of their original diameter (in order to ascertain the success of the welding operation), care being always taken that the weld should be in the centre of the sample. Before and after the mechanical tests, from each sample a portion was taken from the zone of welding, and a portion from the immediately neighbouring zone, for purposes of microscopic examination. In the accompanying Tables I. and II. a summary is given of the experiments and observations made in this first series of researches. A microscopic study of the samples was directed to the zone of welding, including the structure of the portion added for the weld, also the original structure of the metal and its structure in the intermediate stage. This research exhibits clearly the change induced by the process of welding in the mechanical properties of the metal, as also the profound alteration of its structure, as may be seen by comparing Figs. 1 and 2 (enlarged 80 diameters; etching by an aqueous 10 per cent. solution of nitric acid).

The first figure exhibits the structure of the original heated metal (sample 1, Table I., p. 290), and the second the structure of the welded zone (sample 2, Table I.). In this last, the great development which the crystals of copper have undergone will be noted, a development due to the high temperature attained by the fused metal in process of welding. The suboxide formed during this process, and dissolved within the metal, may be observed in the form of little globules disseminated within the crystals. In those samples where, on the contrary, the metal used for the weld consisted of phosphorized copper,

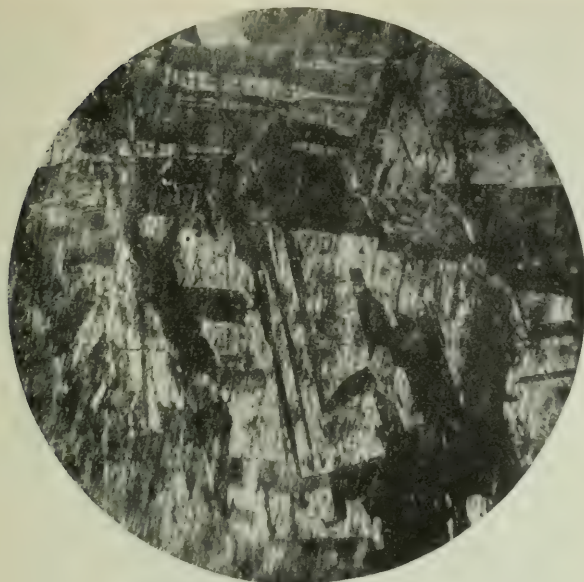


FIG. 1.

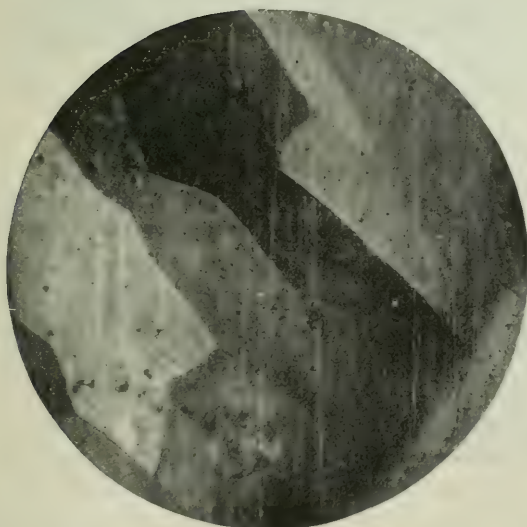


FIG. 2.

the suboxide is practically eliminated; but, coincidently with that elimination, very slight modifications in the mechanical properties of the metal are observable. This shows that the small quantities of suboxide disseminated in the zone of welding have but little effect in the way of modifying the properties of the metal. This difference of structure between the original metal and the metal added in welding may be easily noted by direct observation, without even the aid of the microscope, as is shown by Fig. 3 (enlarged 2 diameters; etching by an aqueous 50 per cent. solution of nitric acid); this is a section of the above-mentioned sample 2 (Table I.), cut from the piece

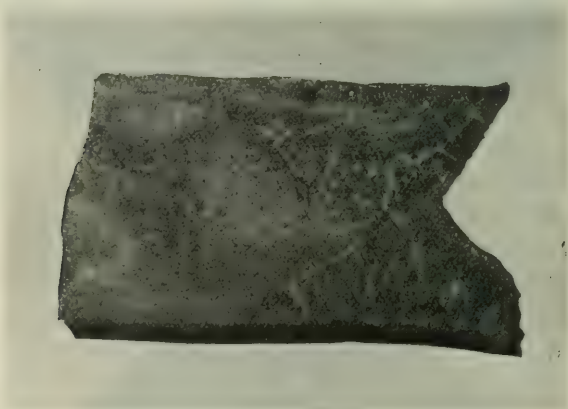


FIG. 3.

subjected to the torsional test, near the zone of rupture. A close examination of this section shows us that the metal was not deformed by the strain to which it was subjected; that the rupture did not take place in the fused and welded zone, but in a neighbouring zone, following the margin of the weld-surface in the original metal that has not undergone fusion. A more minute investigation, while showing continuity between the welding material and the original metal, also reveals in this intermediate zone the presence of innumerable tiny vesicular cavities. They are recognizable even by direct observation of the fractured surface of the sample, imparting to it a peculiar loose granulation apparently due to the

presence of oxide. Fig. 4 (enlarged 80 diameters; etching as usual) shows precisely the characteristic texture of this intermediate zone. At the bottom, the fused portion of the original metal and the welding material is seen to be compact and non-vesicular; on the other hand, cavities are numerous in the zone of metal which has not been subjected to fusion (see the upper part of the figure). The same observation may be extended to all the welded samples of copper in which fracture has taken place, as may be seen in Figs. 5 and 6, representing the fractured surfaces of pieces of welded copper which have been subjected to the torsional and shock tests, compared with sections of exactly similar but non-welded samples. It will be clearly noted how the rupture of the welded samples has taken place along the margin of the chamfer. The explanation of this apparently curious fact is easy enough, if we consider under what conditions the welding of copper takes place. The great thermal conductivity of copper, for one thing, is well known; this conductivity, indeed, is so great as to make the process of welding big masses extremely difficult, if not impossible. We know also how easily that metal absorbs gases at high temperatures. In the oxy-acetylene process of welding, the tongue of the flame is rich in hydrogen and in carbon monoxide, products of combustion

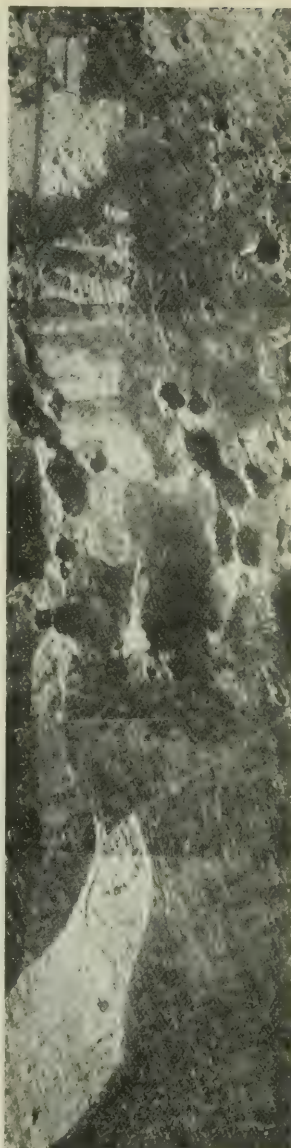


FIG. 4.

which are easily absorbed by the metal during the heating up that precedes fusion, prolonged as it is by the high thermal conductivity of the metal.

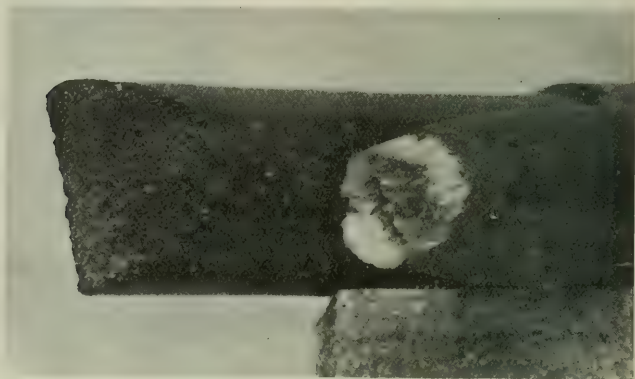


FIG. 5.

When the internal surface of the parts which are to be welded begins to melt, then the metal used for the weld is applied thereto, its fusion taking place with extreme rapidity,

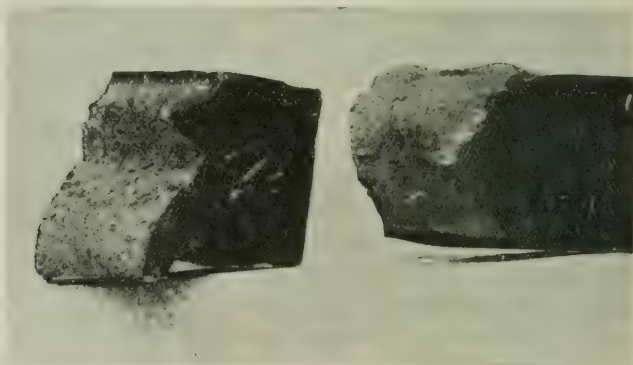


FIG. 6.

the period of heating being much briefer, as the material used consists of fine-drawn wire. Cooling and solidification also ensue quickly; while, from the mass of metal which heated up more slowly, that is, from the original surface of the

chamfer, the gases absorbed in great quantity during the period of heating which preceded the actual welding are eliminated coincidentally with the fall of temperature.

But the elimination of these gases is not complete, as the main mass of the added welding material is at this time quite solidified, and so their occlusion determines the formation of small cavities along the original surfaces of the welded parts, that is, along the surfaces of chamfer. These surfaces, pitted with cavities and considerably oxidized (despite the precautions observed during the process of welding), constitute a plane of weakness when the metal is subjected to strains and stresses, and it is consequently along them that fracture takes place.

The inevitable existence in the zone of welding of a weak surface, of low resisting power, being admitted, it will be easily understood how, when carrying out mechanical processes on the weld, as, for example, by hammering, which are intended to assimilate the structure of the welded portion to the original structure of the metal, we obtain a very low efficiency factor, if not one equivalent to zero. This will be noted on referring to the data set forth in Table I., and for this reason I have not thought it opportune to insist on these mechanical processes in the course of the various series of experiments.

Of greater efficacy, on the other hand, are thermal processes, such as reheating for about half an hour to 750° or 800° C., to which several samples were subjected after welding, as may be gathered from the results set forth in Tables I. and II. A favourable effect on the mechanical properties of the welded metal might be expected from this treatment, as it tends to relieve the strain often set up within the metal during the process of welding, and to restore homogeneity to its structure. We may note in this respect the results obtained from the Brinell tests of hardness (see Table I.).

TABLE I.

No. of Sample.*	Measurements of Sample in Millimetres.	Thermal and Mechanical Treatment.	Average Ultimate Stress. Kgs. per Square Mm.	Average Elongation. Per Cent.	Average Contracted Diameter in Mm.	Average Hardness. Brinell, + 500 Kgs. Ball 10 Mm. Diameter.	Remarks.
1 {	Diameter = 15. Useful length = 150.	Reheated.	23.0	43.4	...	0.38	Not welded.
2	Do.	{ Cooled in air after welding.	{ 10.5	2.6	...	{ 44.5 in the weld.	{ Welded with pure copper; rupture in the weld; fracture coarsely and irregularly granular; vacuoles (small) present.
3	Do.	Do.	12.3	3.1	...	43.0 do.	{ Welded with phosphorized copper; rupture in the weld; medium-grained fracture.
4	Do.	Reheated.	11.3	4.8	...	36.0 do.	Do. do.
5 {	Diameter = 12. Useful length = 100.	{ Not reheated.	{ 24.0	40.0	7.3	54.0	Not welded.
6	Do.	As Sample 2.	12.9	2.0	11.8	{ 35.0 in the weld.	{ Welded with pure copper; rupture in the weld; coarsely granular fracture.
7	Do.	As Sample 4.	13.5	4.5	10.3	34.5 do.	Do. do.
8	Do.	{ Hammered and reheated after welding.	{ 14.2	3.4	11.2	36.0 do.	{ Do., medium-grained fracture.
9	Do.	Do.	13.1	2.8	11.6	40.0 do.	{ Welded with phosphorized copper; rupture in the weld; medium-grained fracture.

* Two samples, prepared and treated in the same way, correspond to each number.

+ The Brinell tests were carried out on samples other than those subjected to the torsional tests.

TABLE II.—*Shock Tests with the Charpy Apparatus on Prismatic Rods, 10 × 10 × 60 millimetres, with semicircular notch half-way down, 2 millimetres deep (distance of supports, 40 millimetres).*

Bob (weight) = 22·45 kilogrammes.
h = 1·3363 metre.

No. of Sample.	Initial Dimensions of the Sample.	Thermal Treatment.	Angle of the Indicator.	Breaking Test. Kgs. Mm.	Remarks.
1 {	Rods, 35 mm. in diameter.	... Reheated. Cooled in air after welding.	110°	8·936	Not welded.
2 {	Do.		109°	9·194	Not welded.
3 {	Do.		139°	2·464	Welded with phosphorized copper; medium-grained fracture.
4 {	Do.	Do.	134°	3·407	Welded with pure copper; coarsely granular fracture.
5 {	Do.	Reheated after welding.	132°	3·807	Do. do.

2. Bronze.

A second series of analogous investigations was carried out on three ordinary types of bronze, which, for the sake of brevity, are here designated as A, B, and C. Their chemical composition was as follows:—

	A.	B.	C.
	Per Cent.	Per Cent.	Per Cent.
Copper . . .	94·2	87·9	87·1
Tin . . .	5·7	11·01	9·3
Zinc	1·53	...
Lead	3·48

The metal was in the form of rods, measuring 25 millimetres (1 inch) in diameter, cast in moulds which had been very carefully dried. As welding material, very thin rods of bronze of exactly similar composition were used.

The experiments were conducted in the same manner as the first series. But we must at once observe that in every case, despite all the precautions taken, innumerable vesicular cavities were formed in the zone of welding over the entire

surface of the weld. For this reason I have thought it advisable to limit investigation to tests of fragility and to microscopic examination: the former were carried out, assuredly not in the expectation of determining with precision the mechanical properties of the metal (more or less modified in process of welding), but in order to ascertain, at all events approximately, how far its resisting power had diminished. In the accompanying Table III. (p. 293) are set forth the results of the experiments and the observations to which they gave rise.

Microscopic examination of the various samples has confirmed the experimental results. The great heat to which the metal is subjected, and the sudden variations of temperature which occur within it during the process of welding and in the course of the subsequent cooling, each play their part in modifying profoundly the structure of the metal in the zone of welding. High temperatures, facilitating the oxidation of the fused metal by means of the action of the oxygen of the atmosphere, determine, in the first place, the oxidation of those constitutive elements of the alloy which have most affinity for oxygen—as, for instance, tin, zinc, and lead. This oxidation reveals itself in the decreased proportion of those elements which in part are volatilized, and in part pass into the slag in the form of oxides; also in the formation of bubbles or vesicles, arising from the partial reduction of these very oxides by the excess of metal (the metallic mass) present; also in the lowering of the mechanical properties of the zone of welding, caused by the innumerable bubbles or vesicles set up within it, and accentuated by the diffusion of tin oxide (SnO_2) in the mass of the alloy, partly in the shape of acicular inclusions.

Moreover, the high temperature attained in the course of the process of welding, with alloys of low tin content (alloy A), in which really a single constituent is present—a “mixed crystals” of copper and tin—determines, as we have seen in the case of pure copper, a commencement of breaking up of the metal, with the consequent formation of big granules. This may be seen in the section reproduced in Fig. 7 (enlarged 2 diameters, etching as usual), which illustrates the welded zone, ruptured by shock, of sample A3 (see Table III.).

Finally, the rapid variations of temperature during the

TABLE III.—*Shore Tests with the Charpy Apparatus.**

Sample No. of	Initial Dimensions of Sample.	Thermal Treatment.	Indicated Angle.	Breaking Test. Kgs. Mm.	Mean Chemical Analysis		Remarks.
					Of the Metal. Per Cent.	Of the Welded Zone. Per Cent.	
A1	Rods, diameter = 40 millimetres.	Rough fusion.	128°	4·646	{ Cu=94·2 Sn=5·7	{ ...	Not welded.
A2	Do.	Reheated.	119°	6·698	Do.
A3	Do.	Cooled in air after welding.	141°	2·112	...	Cu=94·89	Welded; medium-grained fracture, with small vacuoles.
A4	Do.	Reheated after welding.	132°	3·807	Welded; medium-grained fracture, with vacuoles.
B1	Do.	Reheated.	134°	3·407	{ Cu=87·9 Sn=11·01 Zn=1·03	{ ...	Not welded.
B2	Do.	Cooled in air after welding.	140°	2·286	...	{ Cu=90·2 Sn=9·01 Zn=0·8	Welded; finely granular fracture, with numerous vacuoles.
B3	Do.	Reheated after welding.	139°	2·464	Do. do.
C1	Do.	Reheated.	136°	3·019	{ Cu=87·1 Sn=9·3 Pb=3·48	{ Cu=89·7 Pb=2·9	Not welded.
C2	Do.	Cooled in air after welding.	145°	1·457	Welded; finely granular fracture, with numerous vacuoles.
C3	Do.	Reheated after welding.	139°	2·464	Do. do.

* See Table II.

process of welding, determine—in the case of bronzes of higher tin content, wherein two constituents are present, namely, the α and β mixed crystals of copper and tin—an irregular and very conspicuous subdivision of these constituents, imparting to the metal a heterogeneous structure. This will be seen on referring to Fig. 8 (enlarged 80 diameters, etched with a 4 per cent. hydrochloric acid solution of ferric chloride), which illustrates the structure of the zone of welding of sample B2 (Table III.). Here we see clearly the minutely irregular distribution of the solid solution β , which is made the more manifest by comparison with Fig. 9, representing the well-

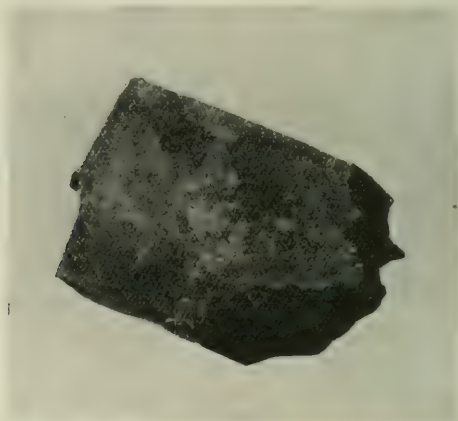


FIG. 7.

developed homogeneous structure of the original reheated metal (sample B1, Table III.).

The localization of the surface of fracture in the samples of welded copper to the margin of the chamfer is again observed in the case of the zone of welding of bronzes, as we may satisfy ourselves from inspection of Fig. 10, which represents the zone of fracture of the welded sample C2, and by comparing it with that of the unwelded sample C1 (Table III.). The consequent structural modification, partly analogous to that undergone by copper, is illustrated in Fig. 11 (usual enlargement, usual etching), which represents the passage-zone between the fused welding material and the original

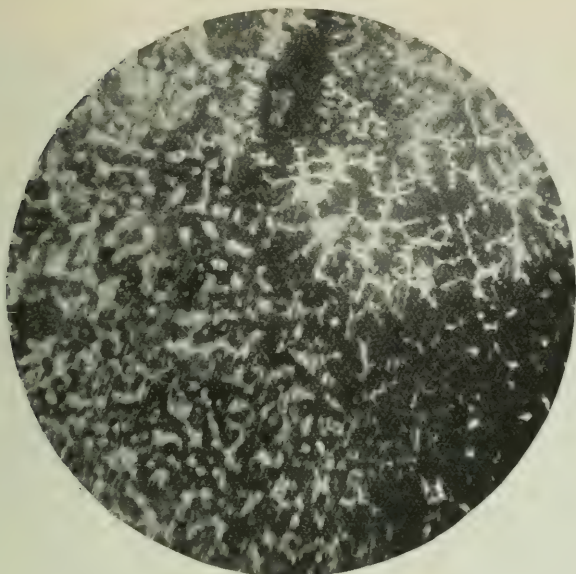


FIG. 8.

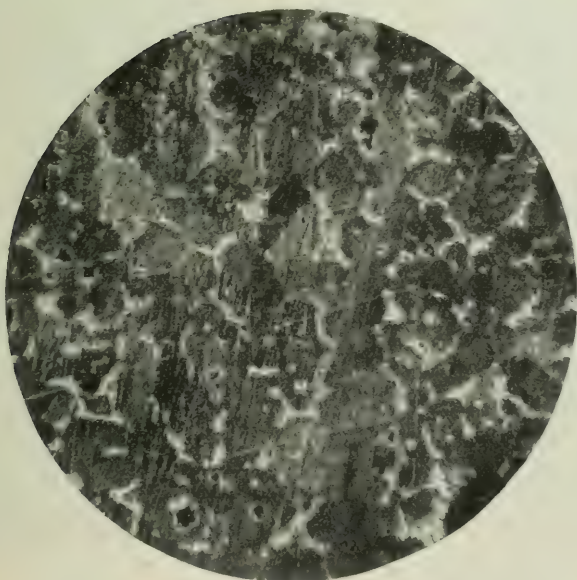


FIG. 9.

surface of sample C2 (Table III.). Towards the top of this figure we notice numerous blowholes, while these are absent in the fine-textured welding material, made up of small *insule* of lead and of solid solution β , immersed in a mass of solid solution α .

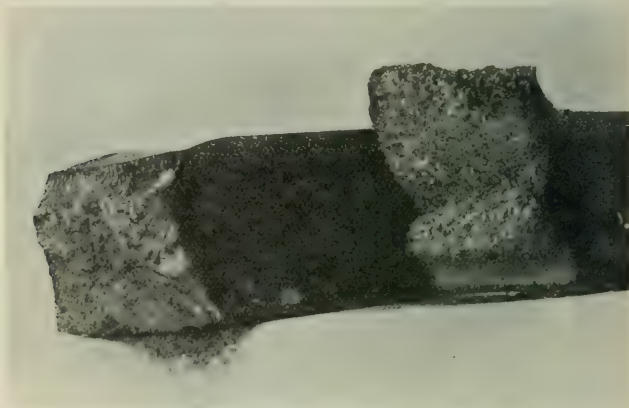


FIG. 10.

Admitting all that precedes, we may reasonably expect that an appropriate reheating of the welded portion will prove even more efficacious than in the case of copper, because, in addition to relieving the internal strains of the metal set up by the process of welding, it tends to restore to it an improved homogeneity of structure.

3. *Brass.*

A third series of experiments was conducted, by the same methods as the two series already described, with the types of brass fusible at high temperatures, here designated respectively as M and N. Their composition is as follows:—

	M.	N.
	Per Cent.	Per Cent.
Copper	60.2	55.18
Zinc	40.08	41.50
Manganese	3.2

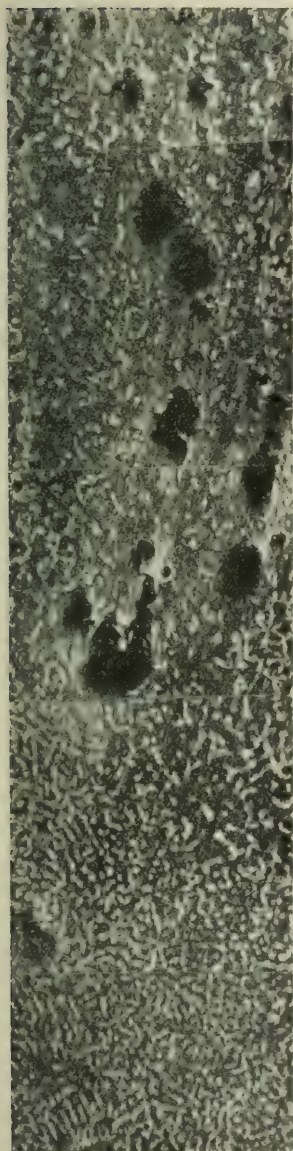


FIG. 11.

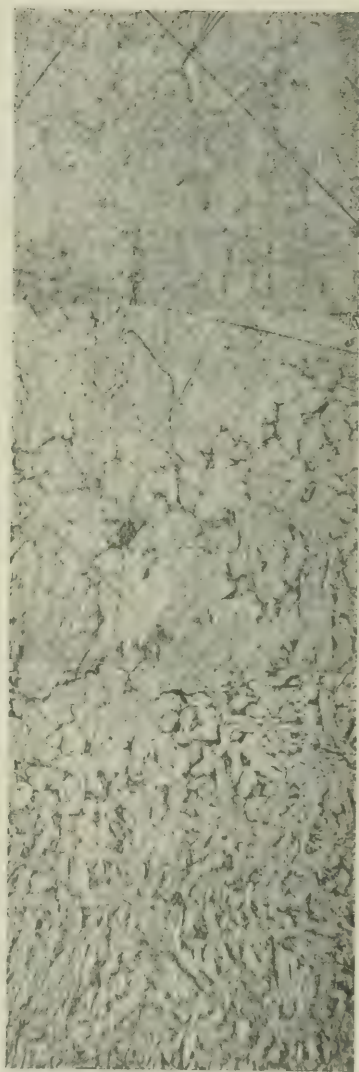


FIG. 12.

The first mentioned was cast in rods, measuring 30 millimetres ($1\frac{1}{5}$ inch) in diameter, in perfectly dry moulding material; the other was wire-drawn into rods, 25 millimetres (1 inch) in diameter. The welding material consisted of very thin rods, in each case of exactly the same composition as the original alloy.

The phenomenon of the unwelcome vesicles, set up in large numbers within the welding zone, despite all the preventive precautions that could be taken, was intensified in the case of these alloys by the extreme facility with which the zinc contained in the metal oxidizes. In the accompanying Table IV.

TABLE IV.—*Shock Tests with the Charpy Apparatus.**

No. of Sample.	Thermal Treatment.	Indicated Angle.	Breaking Test, Kgs. Mm.	Mean Chemical Analysis		Remarks.
				Of the Metal, Per Cent.	Of the Weld-Zone, Per Cent.	
M1	Reheated.	128°	4·646	Cu=60·2 Zn=40·08	{ ...	Not welded.
M2	Cooled in air after welding.	141°	2·112	...	Cu=69·3	Welded; finely granular fracture; numerous vacuoles.
M3	Reheated after welding.	138°	2·646	Do. do.
N4	Reheated.	128°	4·646	Cu=55·18 Mn=3·2	{ ...	Not welded.
N5	Reheated after welding.	140°	2·286	...	Cu=68·75 Mn=1·2	Welded; medium-grained fracture; numerous vacuoles.

are set forth the results obtained from shock tests and from chemical analysis of the various samples.

Microscopic examination, confirming the results here tabulated, leads to the same conclusions as those postulated in regard to the bronzes. In order, therefore, to avoid needless repetition, I will content myself with referring the reader to what has already been said on that point. We may note, however, in these alloys a diminution in the capacity, when

* See Table II.

heated, of absorbing the products of combustion of the welding flame; coincidently with this diminution, the liability of the welded parts to fracture along the margins of the chamfer decreases. In confirmation of the results yielded by chemical analysis, Fig. 12 (usual enlargement, simple etching) reproduces the structure of the passage-zone between the original metal and the fused welding material (sample 2, Table IV.); while in the former, towards the top of the figure, we observe the typical structure of the alloy, consisting of mixed crystals of the solid solutions α and β ; in the latter we note the presence of a single constituent, the solid solution α , resulting from the considerable decrease in the percentage of zinc revealed by chemical analysis. In this portion of the metal, numerous inclusions of oxide of zinc, formed in the course of the welding process, are to be seen.

CONCLUSIONS.

The results obtained and the observations recorded in this triple series of investigations concerning the oxy-acetylene autogenous welding of copper and its chief alloys demonstrate—

(1) That rapid heating and sudden fusion of the metal subjected to welding profoundly modify its physical and mechanical properties, developing within it internal strains and structural alterations which are of detrimental effect.

(2) That the structural modifications which take place in the process of welding, apart from the alterations in composition of the metal, may be classified under two principal headings: (i.) coarse crystallization of a single-constituent metal, and (ii.) minutely heterogeneous structure of an alloy consisting of two or more elements. We must also take into account the discontinuity of structure attaching to metals in which there are oxide inclusions or blowholes.

(3) That the deficiency in mechanical properties, most conspicuous in all that regards the tenacity and elasticity of a metal, is expressed in the case of copper by an average reduction of 50 per cent. in the capacity to resist fracture, and an increase of about 30 per cent. in brittleness, while the percentage ductility is reduced to about a tenth of the original.

In the case of bronzes and brasses, the deficiency in mechanical properties is not susceptible of the closest measurement, but it is greatly intensified and proportionately detrimental as the number and variety of the constituents of the alloy subjected to welding are increased.

(4) That, while mechanical treatment, such as hammering along the zone of welding, has practically no useful effect on the properties of the welded metal, thermal treatment, such as reheating, prolonged for a suitable interval at a fixed temperature, exerts an undoubted ameliorative influence, since in the first place it relieves the latent internal strain set up by the sudden temperature-changes involved in the process of welding, and in the second place it restores homogeneity to the structure of the metal itself. Consequently, and more particularly in the case of alloys made up of several constituents, the conditions of cooling of the welded metal are of special importance, the slower the cooling the greater being the ameliorative effect.

(5) That considerable variations—diverse according to the manner in which the process of welding is applied—occur in the composition of bronzes and brasses; these variations are the more extensive the greater is the number of constituents of which the alloy is made up, and also in proportion to the affinity of these constituents for oxygen and to the volatility of the oxides formed therefrom. Thus, for example, in the bronzes of type B (Table III.), in the welded zone, there is an average diminution of 19·0 per cent. in the proportion of tin; while the loss of zinc, a more easily oxidized metal than tin, amounts to 22·3 per cent. (the original proportion present being smaller than that of tin). In brasses, wherein the percentage of zinc is much higher, its decrease in the welded zone amounts to 28·7 per cent. We must also bear in mind that the oxides thus formed have a tendency to be absorbed easily into the metal, modifying profoundly its properties. In pure copper subjected to the welding process changes in chemical composition cannot be traced, as the metal is made up of a single constituent; and it is only affected deeply by oxidation when the necessary precautions have been omitted in the process of welding, the suboxide then formed diffusing with great facility into the copper.

(6) That taking into account the results obtained and the conclusions here postulated, we may assert that the oxy-acetylene autogenous welding of copper and its principal alloys has a practical application, limited to those parts of machinery which are not of large dimensions and are not subjected to severe mechanical stresses.

SECOND GROUP.

OXY-ACETYLENE AUTOGENOUS WELDING OF ALUMINIUM.

The experiments on this group were carried out with two types of metal, one designated by the letter S (see Tables V. and VI.), consisting of commercially pure aluminium containing 99 per cent. of the metal,* in the form of rods of two different diameters (30 and 12 millimetres respectively) and of flat bars, 6 millimetres thick; the other, designated by the letter T (see Table V.), in the form of rods, 15 millimetres in diameter, consisting of aluminium alloyed with 3 per cent. of copper (a type of alloy in common use industrially). The welding material consisted of thin rods of metal of identical composition with S and T respectively. The experiments were conducted under precisely the same conditions as those of the previous series, especial care being taken to avoid oxidation, to which the metal is so easily liable during the process of welding. For this purpose appropriate deoxidizing powders were used. In the accompanying Tables V. and VI. the results obtained are set forth in detail.

Micrographic study of the several samples, pursued by the same method as that followed in the foregoing series of investigations, enabled one to identify without difficulty the welding zone by its coarsely granular structure. This structure is a consequence of the high temperature attained by the metal in fusion, and is illustrated in Fig. 13 (enlarged 80 diameters; etching by an aqueous 10 per cent. solution of caustic potash). This represents the weld-zone of sample S7 (see Table V.); the thin, dark filaments or threads which it reveals are the margins of the big crystals, while within the crystals themselves are seen small, and exceptionally numerous,

* Kindly supplied by the British Aluminium Co. Ltd., London.

TABLE V.

* No. of Sample.	Mean Dimensions of Sample in Millimetres.	Thermal and Mechanical Treatment.	Average Ultimate Stress, Kgs. per Square Mm.	Mean Elongation up to Breaking Point, Per Cent.	Contraction.	Cold Bending Tests on the Weld-Zone.	Remarks.
S1	Diameter = 16; useful length = 100.	12.7	16	8.3	...	Not welded.
S2	Do.	Reheated.	11.5	18.5	7.8	...	Do.
S3	Do.	Cooled in air after welding.	5.4	4.3	14.5	...	Welded; rupture at the weld; fibrous fracture with vacuoles.
S4	Do.	Reheated after welding.	8.6	5.1	13.2	...	Same as above, but fracture oxidized. Vacuoles not mentioned.
S5	Diameter = 8; useful length = 80.	16.8	10.0	4.0	...	Not welded.
S6	Do.	Reheated.	14.2	16.1	3.2	180°	Not welded.
S7	Do.	Cooled in air after welding.	7.6	4.0	7.0	180°	Welded; rupture at the weld; fibrous fracture.
S8	Do.	Reheated after welding.	7.0	8.8	6.5	...	Do.
S9	Do.	Hammered after welding.	8.2	5.1	6.3	180°	Do.
S10	Do.	Hammered and reheated after welding.	8.6	15.6	5.5	...	Do.
S11	20 x 5. Useful length = 100.	12.0	7.2	16.8 x 1.9	...	Not welded.
S12	Do.	Reheated.	11.4	14.2	16.9 x 3.5	180°	Do.
S13	Do.	Reheated after welding.	7.7	9.2	18.2 x 3.2	...	Welded; rupture at the weld; fibrous fracture.
S14	Do.	Hammered and reheated after welding.	9.2	17.5	16.5 x 2.5	180°	Do.
T15	Diameter = 10; useful length = 100.	18.5	13.5	6.5	...	Not welded.
T16	Do.	Reheated.	15.8	18.1	7.0	...	Do.
T17	Do.	Cooled in air after welding.	5.0	0.9	10.0	...	Welded; rupture at the weld; coarsely granular oxidized fracture; vacuoles.
T18	Do.	Hammered and reheated after welding.	7.2	2.1	9.7	...	Welded; rupture at the weld; medium-grained fracture; vacuoles.

* Two samples prepared and treated in identical fashion correspond to each number.

dark, rounded inclusions—less abundant in the other samples—formed by the oxide which has remained imprisoned in the metal. In this case oxidation was especially active during the process of fusion. This structure, which repeats itself in the various samples of type S, undergoes modifications varying according to the different treatment to which the metal is subjected. Hammering, for instance, tends to approximate the structure of the weld-zone to the original texture of the metal; while reheating tends to make the texture of the entire weld-zone homogeneous, eliminating the internal strains set up within the metal as a consequence of rapid fusion and similarly rapid cooling.

TABLE VI.—*Shock Tests with the Charpy Apparatus.* (See Table II., p. 291.)

No. of Sample.	Initial Dimensions of Sample.	Thermal and Mechanical Treatment.	Indicated Angle.	Breaking Test. Kgs. Mm.	Brinell Hardness (average), 500 Kgs.	Remarks.
S1	Rods, 20 mm. in diameter.	...	117°	7·181	...	Not welded.
S2		Reheated.	110°	8·936	27·2	Not welded.
S3		Cooled in air after welding.	141	2·112	...	{ Welded; medium-grained fracture; small vacuoles.
S4		Reheated after welding.	119°	6·698	{ 25·9 in the } { weld. }	{ Same as above, but no vacuoles.
S5		Hammered and reheated after welding.	128°	4·646	27·2	Do. do.

In contradistinction to the phenomena observed in the case of copper, the oxy-acetylene autogenous welding of pure aluminium results in an intimate union between the latter and the welding material, the two substances forming an inseparable *corpus*, as is shown by bending and torsional tests (in the cold). This is clearly seen in Figs. 14 and 15: the former shows a section polished, then etched with a hydrochloric acid solution of ferric chloride, of the weld-zone of a sample which has undergone the above-mentioned bending test. In it no discontinuity of the metal can be traced, nor any inclusions of slag; and we can only note the coarse crystallization charac-

teristic of the metal when subjected to very high temperatures. The second figure (15), on the other hand, shows on the left, in the fracture-zone of a welded sample ruptured in the torsional test, undoubted deformation of the metal in the neighbourhood of the fracture-surface: this deformation being, however, actually less marked than in the original non-welded metal (on the right of the figure) is an additional proof of the complete and intimate union of the welded portions. These observations are confirmed also by the contraction which takes

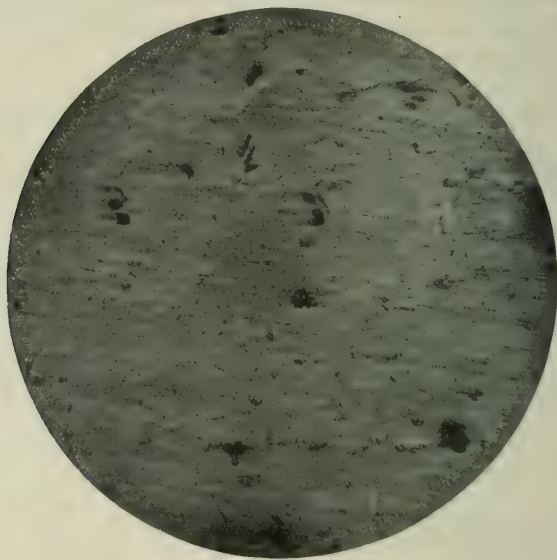


FIG. 13.

place in the fracture-zone of the welded metal subjected to the torsional test, and by the high coefficient of quality recorded in the case of the welded samples (see Table V.). We must bear in mind, however, that the values obtained as a result of tests carried out on samples of considerable dimensions (see Table V., 3 and 4) are somewhat low, on account of the difficulty of obtaining a perfect weld in the innermost portions of the chamfer. The results yielded by the tests carried out with the second type of aluminium (type T), alloyed with 3 per cent. of copper, tend to prove by the low values obtained



FIG. 14.

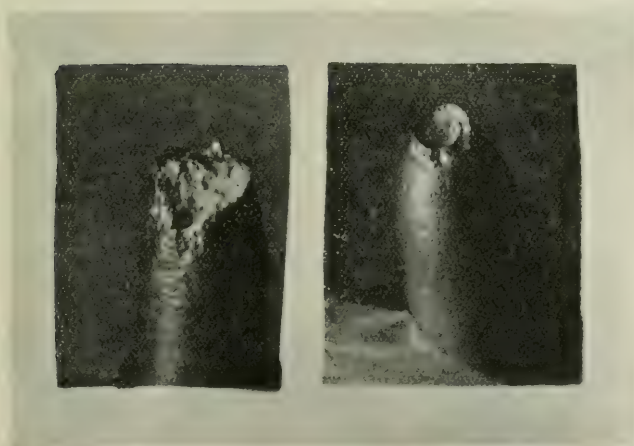


FIG. 15.

that the addition of copper to the aluminium facilitates oxidation of the metal during the process of welding, the complete success of which cannot, therefore, be guaranteed.

CONCLUSIONS.

The data accumulated and the observations made in the course of this series of experiments with the oxy-acetylene autogenous welding of aluminium, show—

1. That sudden heating and rapid fusion of the metal subjected to the welding process alter its physical and mechanical properties in a manner analogous to that observed in the case of copper, though in less degree. They set up within the metal latent internal strains, and modify its structure detrimentally.

2. That the structural modifications, induced by excessively rapid heating during the process of welding, take the form of coarse crystallization of the metal.

3. That, so long as all the necessary precautions are observed in the process of welding, the changes in the mechanical properties of pure aluminium, such as breaking strain, ductility, hardness of the weld-zone, are not very profound, although a notable increase in brittleness is observable, as is shown by the results of shock tests. The presence of copper, however, modifies profoundly in a detrimental sense the mechanical properties of aluminium.

4. That, in consequence of the feasibility of achieving with pure aluminium a perfect and homogeneous weld of the metal, both mechanical (hammering) and thermal (reheating to 450° to 500° C.) treatment is extremely efficacious, in that it sets up greater homogeneity in the weld-zone, and eliminates the effect of the excessively rapid heating undergone in process of welding, ameliorating consequently the quality of the metal.

5. That whenever aluminium contains small quantities of other elements easily oxidizable at high temperatures (as, for example, copper), the oxidation of the metal in fusion is facilitated, also the inclusion within it of granules of oxide detrimental to the mechanical properties of the weld-zone.

6. That, taking into account the results obtained, as also the foregoing conclusions, we may assert that the oxy-acetylene autogenous welding of aluminium, when carried out with the necessary precautions, is capable of extensive application in practice, especially for the autogenous welding of small machine parts.

JOINT DISCUSSION.

Mr. F. JOHNSON, M.Sc. (Birmingham), said that Mr. Tucker stated on page 266 that when brazing solder, containing as little as 0.5 per cent. of tin, was used for brazing bicycle frames he had found that the joints were very unsatisfactory and unsafe. He (Mr. Johnson) pointed out in a short paper,* read at the last meeting, that tin in brass, particularly of a composition which was usually attained after the application of a brazing solder, separated out from the brass in the form of a brittle eutectoid, and he thought the brittle nature of the joint was directly attributable to the presence of that brittle SnCu_4 eutectoid.

Dr. WALTER ROSENHAIN (Member of Council) desired to make a few remarks on the general subject of welding in non-ferrous metals. He had recently had the pleasure of listening to a paper by an eminent French engineer, which dealt with a large number of welds carried out on the lines of some of the autogenous welding which had been referred to in the paper; and he came to the bold conclusion that in every case where fracture tended to endanger life or cause serious injury welding must be entirely prohibited. In an international gathering of a large number of experts that conclusion raised a storm of demur. They were told that anchor chains and welded steam-pipes were things the breakage of which entailed danger to life, and yet they were being made in large numbers. It was pointed out in reply that the stresses on those articles were, as a rule, extremely small. While hardly associating himself with the sweeping dictum of M. Frémont, he thought the members would be right in being extremely careful in placing any reliance upon welding where serious stresses had to be resisted. A large number of tests of various kinds of welds had been undertaken in connection with iron and steel, an account of which had been given by Mr. Law and Mr. Merrett, and a large number of mechanical tests with welds had been systematically undertaken at the National Physical Laboratory; the net result of which was in strong confirmation of Dr. Carnevali's contention, that the process almost inevitably resulted in injury to the metal, not so much at the point of the weld, but just beyond it. What really happened was that the metal was being overheated in order to weld it. In some cases it might be possible to apply work to the metal at the weld itself, but just beyond the point where the weld had taken place, unless very great precautions had been taken of thickening up the metal first and reducing it afterwards, there was an overheated structure which was dangerous, from which failure might result at any time. He thought 50 per cent., as Dr. Carnevali had stated, was by no means an exaggeration of the weakness caused in some of the cases. Although autogenous welding might be an extremely useful process for the purpose of repair and construction where tightness against gases and liquids under small pressures only had to be taken into consideration,

* *Journal of the Institute of Metals*, No. 1, 1912, vol. vii. p. 203.

it was a dangerous process if it was applied to parts which had to carry stress, particularly working parts of machinery. That was a point which those whose business it was to push processes of autogenous welding were a little apt to forget at times.

Mr. E. F. LAW, Assoc.R.S.M. (London), desired to bear out the remarks Dr. Rosenhain had just made with regard to the question of welding. Where it was of importance to life and limb he thought welds should be accepted with the utmost caution. There was no doubt that if a weld was properly made by means of the processes referred to it would give excellent results. He said, advisedly, "If properly made." Unfortunately many did not receive the care which they should, and it was exceedingly unfortunate that there was no way of telling beforehand whether the weld was good or not, except by testing the articles to destruction. That was the weak point of all the welds.

Mr. E. I. THORNE (London) said the first point with which he intended to deal had already been referred to by Dr. Rosenhain, namely, with reference to the question of joining aluminium with a rich alloy, composed chiefly of aluminium itself. It would be found by reference to page 270 that the joint had been very well made and had withstood the steam test. He quite agreed with Dr. Rosenhain that the hot water test was quite as good if not better. He had personally made many tests of aluminium alloys in the joining up of aluminium by those means, and he did not think there was any solder of any kind that would successfully withstand the hot water test where the joining metal was composed largely of some other element than aluminium. The chief point, however, was, What was the value of the test to the manufacturer? It was all very well to test a sample, to hand it over and say that it was of no use; but what was the relation between the length of time it would stand that hot water test, and the length of time the joint would remain strong under the varying conditions of exposure which exist in practice? That was a point which he had not seen laid down anywhere, but it was a point which would be of very great service both to the manufacturer and the user. So far as compound strip was concerned, he was afraid he was somewhat like *Oliver Twist*, because he would like a little more information on the subject. On page 279 reference was made to the process of the manufacture of silver plate by the introduction of a saturated solution of borax, where the silver was practically brought to a molten condition. He would be glad to know whether any similar process was in existence for the manufacture of compound strip, such as nickel on steel, or copper on steel, or an alloy of those two metals on steel. He knew that, in an experimental way, borax could be made to unite nickel or one of the alloys on steel. With regard to the use of aluminium, was it necessary to have the aluminium mixed with a flux, such as was referred to on page 280, or could the joining be done by means of aluminium alone? Many things could be done in the laboratory which could not be done in practice, and the paper was, he thought, rather weak in details in

connection with the manufacture of compound strip. He ventured to think that temperature played a most important part in the question. The statement was made on page 280 that the metals were not melted, but only slightly heated, but on reading further one was left in considerable doubt as to what was intended to be conveyed by "slightly heated." He would like the author to give further particulars on the temperature question if possible. With regard to the use of the sulphide of a metal in admixture with aluminium powder, he would like to know what became of the sulphur. He took it that the sulphur passed over to the aluminium or to the flux, but could they be quite sure that in every case the sulphur was got rid of, because he thought the sulphur would very deleteriously affect such metals as nickel. He would also like to know whether any method such as burning on was applicable to the manufacture of compound strip. It had been made in an experimental way by casting steel into a sand mould lined with strips of the other metal. He would like to know if the author could tell him if such a method was used commercially, or in any way at all. It would have been interesting if some reference had been made in the paper to the uses to which compound strips were put. One particular use with which he was acquainted was the manufacture of bullet envelopes, and several continental countries were making use of such an alloy for that purpose.

The PRESIDENT said he was sure the members were extremely sorry that neither of the authors of the papers were present, because the results which each of them obtained differed considerably. For instance, Mr. Tucker gave a tenacity of 95 to 97 per cent. in the case of welded copper against that of ordinary copper rods which were not welded. On the other hand, Dr. Carnevali gave results of only about 50 per cent. It was extremely difficult to reconcile those two contradictory results. He wondered whether they arose from the use of different mixtures of oxygen and acetylene, because Mr. Tucker especially pointed out that it was necessary to use an excess of oxygen if satisfactory results were desired. Several remarks had been made with regard to welding and brazing, deprecating the use of either in cases where the metal had to be subjected to severe stress. He was entirely in agreement with those speakers. He thought no tube ought to be permitted to be used for high pressure steam if it was a brazed tube. Brazing ought to be entirely given up for tubes which had to stand a very high steam pressure, not because the joint itself was not strong, but because when the process of brazing was carelessly performed, as it too often was, the structure of the copper near the brazed part was more or less altered. The flame which was used was generally of a reducing character, hence the copper in the neighbourhood of the joint was rendered brittle. Autogenous welding was sometimes spoken of as being modern, yet the first people who were autogenous welders were the Romans, one or two centuries B.C. He had examined several Roman lead pipes which were dug up in this country, and found they had been made by autogenous welding. A strip of metal had been hammered out; it had then been bent in the form

of a cylinder with the edges of the metal recurved, and in the hollow formed between the recurved edges excess of lead had been poured in at a high temperature until there was a perfect joint. Curiously enough the Romans never used that process except for underground work. They had the same solder that was used at the present day, a fact he had verified from examining several specimens of it. It differed only 1 or 2 per cent. from what used to be called the sealed solder of the Plumbers' Company. Tubes which were not below the ground, the Romans frequently soldered with solder; but for all underground work they adopted the system of autogenous welding. In Japan the system of burning on was very extensively practised. In bronze foundries the vases and ornamental objects which were cast were always cast in very simple forms, and the handles or projecting ornaments were always burnt on. The papers by Dr. Carnevali and Mr. Tucker were the last two papers on the Agenda for discussion, and although both the authors were absent, he was sure the members would desire to accord them a most hearty vote of thanks, and at the same time express their regret that neither of them had been able to be present to read the papers, or to reply to the discussion.

The resolution of thanks was carried by acclamation.

COMMUNICATIONS.

Mr. J. L. HAUGHTON, M.Sc. (Birmingham), wrote that the nomenclature of the solid solutions occurring in the bronzes that Dr. Carnevali investigated was not in conformity with that usually adopted. The two solid solutions existing at atmospheric temperatures in the author's bronzes "A" and "C" would be α and δ , not α and β ; a glance at Fig. 9 showed the characteristic $\alpha + \delta$ complex in a matrix of α . At the temperature of welding, doubtless, α and β were present, but not, as stated on page 294, in the cold alloy.

Mr. F. JOHNSON, M.Sc. (Birmingham), wrote that he was particularly interested in the first group dealt with by the author, viz. that treating of the welding of copper and its principal alloys. He was not surprised to learn that the difficulties in the way of successfully welding pure copper were practically insuperable. The author had well outlined these difficulties, viz. :

- (1) The great thermal conductivity of copper, obviating the possibility of getting the necessary local intensity of heat at the weld.
- (2) The ease with which copper absorbs gases at high temperatures.
- (3) The ease with which copper oxidizes and dissolves its own oxide at high temperatures.

On page 286 the author showed that the small amount of oxide disseminated in the zone of welding had little effect on the mechanical properties. Subsequently he showed that a welded sample when subjected to the

torsional test did not rupture at the weld, but in a neighbouring zone in which fusion did not occur. Hence the presence of the vesicular cavities in that zone could not be due, as the author stated, to the occurrence of oxide, but to the absorption of reducing gases, hydrogen and carbon monoxide. The action of the metal on any excess acetylene would probably be to decompose it into hydrogen, which the metal would absorb, and carbon.

The author's explanation of the formation of blowholes in the welded bronzes (page 292) was rather open to dispute. That the oxides of the metals could be reduced again by the metallic mass of the bronze was impossible. That they could be partially reduced by the gaseous products of combustion of the acetylene with the formation of new gases such as carbon dioxide, and their subsequent occlusion, was extremely more likely. It was also possible that the cavities were due to mechanically entangled oxides, and not necessarily in every case to occluded gas.

Mr. TUCKER wrote, in reply to the discussion, that he wished, first of all, to express to the Institute his regret that a critical illness in his family prevented him from reading his paper.

Mr. Johnson had mentioned that the presence of tin in a brazing solder gave rise to the separation of a brittle eutectoid, which might be the reason of the weak joint invariably found when such solder was used, but his (Mr. Tucker's) experience was that the substance of the steel was affected, the tin, though very small in amount, seeming to act with the same extremely pernicious influence as obtained under other conditions; in fact, probably both sets of causes were at work, *i.e.* (1) the weakness caused by Mr. Johnson's eutectoid, and (2) the deterioration of the steel itself on account of the presence of the tin.

He agreed entirely with the remarks of Dr. Rosenhain as to the serious responsibility attending the use of autogenous welding in cases where the parts were subjected to considerable mechanical strain. When autogenous welding was first introduced advertisements showed that its application was invited for welding up broken crank shafts for motor cars and other engines—a quite absurd proposition—as he had known such welds fail the first time the engine was used. It was pushing the claims for autogenous welding much too far to attempt anything of the kind, but that a very considerable tensile strength was obtainable in auto welding was shown by its regular use for chain-making, as obtained in the Cradley district and elsewhere, also its use for steam-pipe work, under certain restricted conditions, was invaluable.

In reply to Mr. Thorne, thin nickel and copper compound sheets were generally made by deposition on the metal—frequently steel—with subsequent rolling and finishing. There was no difficulty in welding nickel or copper to steel with fluxes, as both metals would alloy with iron, and when thick layers were required that was the method adopted. He did not think that any flux was used with the aluminium powder referred to, nor would it appear to be required with clean surfaces in a reducing atmosphere. The union was very perfect, and the sheets were afterwards made into domestic articles by deep stamping or spinning. He

regretted that he was not able to give the temperatures at which the joining was effected, but it seemed to cover a wide range, and probably the effect of rolling was as great as that of the heat employed. With respect to the use of an oxide or sulphide of a metal which it was intended to unite to another, he held that the oxide or sulphide of aluminium was squeezed out with the flux when the whole was passed through the rolls. With respect to the "burning on" as a method of production of compound metals, he had seen articles of copper and steel in which the copper was in one case the core and in the other the envelope, and both had been made by running steel in a mould containing the copper core or envelope. The use of those compound metals, where costs permitted, was extensive, as it provided on the one hand the strength of the steel or other metal and the immunity from tarnishing of the second metal, and, on the other hand, high conductivity of current or heat together with mechanical strength.

With regard to the President's criticisms of his paper, he thought that it might be anticipated that the results of autogenously welding copper would always be more satisfactory than those of steel or brass, as internal strains would be less likely to arise in the case of a pure and highly conductive metal like copper, where there were no gamma or delta constituents to cause complications. The point the President raised as to the general weakness of such welds was confirmed and amplified by his (Mr. Tucker's) figures, which showed that the thicker the material welded the greater was the internal weakness of the parts adjacent to the actual weld.

SECTION II.

ABSTRACTS OF PAPERS

RELATING TO THE NON-FERROUS METALS AND THE INDUSTRIES CONNECTED THEREWITH.

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THE PROPERTIES OF METALS AND ALLOYS.

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I.—COMMON METALS.

Action of Seltzer Water on Aluminium.—It is found by A. Barillé* that seltzer water acts slowly on aluminium, forming a flocculent precipitate, but, as the product is non-poisonous, aluminium is recommended for siphon heads, if lined with porcelain.

Aluminium as a Water Softener.—In the *Journal* of the Metallurgical and Mining Society of South Africa, March 1912, W. Cullen† describes his experiences with the so-called “Luminator.” He found that its use softened a very hard scale already formed in a boiler, and that the subsequent formation of scale was much reduced.

Blisters on Rolled Copper.—It is stated by W. Stahl‡ that warts or nodules on rolled copper are usually due to holes in the roll surface. They are completely removed by passing several times through smooth rolls. Blisters with a very thin wall are due to overheating of the copper, the metal becoming so soft that the absorbed gases escape. Blisters of this kind may be distinguished by the pure copper colour of thin smooth inner surfaces. Other blisters, due to a bad cast, differ from these in having dark or red linings. Long thread-like cavities indicate porosity in the original ingot.

Density and Coefficient of Expansion of Aluminium.—The density and coefficient of expansion of aluminium of known purity have

* *Journal de Pharmacie et de Chimie*, 1912 [vii.], vol. vi. p. 110.

† *Metallurgical and Chemical Engineering*, No. 6, June 1912, vol. x. p. 351.

‡ *Metallurgie*, 1912, vol. ix. p. 418.

been redetermined by F. J. Brislee.* Metal was obtained from (1) The Société Electrometallurgique Française, and (2) The British Aluminium Company, and was found to have the following composition on analysis :—

	S.E.M.F. (Per Cent.)	B.A. Co. (Per Cent.)
Silicon	0·26	0·25
Iron	0·26	0·23
Aluminium	99·48	99·52
Totals	100·00	100·00

Determinations of density on cast and wrought material gave 2·708 † as the most probable value for cast metal and metal upon which a large amount of work had not been done. The value 2·72 † was obtained in some instances, but was not found for hard-drawn wire. Remelted aluminium gave a value of 2·6821. †

Other determinations carried out later on cold-drawn wire and cold-rolled sheet tended to favour the lower value, 2·708, † which the author is at a loss to explain, and the effect of work on the density of aluminium is being further investigated.

Determinations of the coefficient of expansion gave the following results as means :—

Hard-drawn aluminium	$24·32 \times 10^{-6}$
Annealed aluminium	$24·54 \times 10^{-6}$

between the limits 0° to 100° C.

In the discussion R. Seligmann pointed out that 2·67 is the generally accepted value for the density of aluminium.

Disadvantages of the New American Standard Copper Specification.—This standard specification is deprecated by E. A. Lewis ‡ on the grounds that whilst copper of such a high degree of purity is eminently desirable for such uses as high conductivity wire, it is quite unsuitable for the purposes of the coppersmith. A large amount of work has been done of late years on the properties of various kinds of copper, as, for instance, the researches of Roberts-Austen, Dean's work on firebox plates, an investigation by the author on the effects of impurities on deoxidized commercial copper, the work of F. Johnson on tough-pitch copper, &c.; and in the face of such papers it is difficult to understand how any committee represent-

* *Transactions of the Faraday Society*, June, vol. vii. (3), pp. 221-228.

† Corrected for water at 4° C., and vacuum weighing.

‡ *Metallurgical and Chemical Engineering*, No. 9, September 1912, vol. x. pp. 540-543.

ing makers and users of copper should recommend for all purposes a copper of 99·88 per cent. purity.

It is impossible to work pure copper, and to apply the conductivity test to metal for use as sheet, tubes and rods, and ingots for the manufacture of brass for rolling is valueless and misleading; bending, opening, swagging, tensile tests, and chemical analyses for the purpose of limiting impurities are the tests which should be used in such cases. None of these appear in the above specification.

The metals and non-metals which may be present in refined or manufactured copper, either as impurities or intentionally added, are lead, bismuth, antimony, tin, arsenic, zinc, manganese, nickel, phosphorus, silicon, and oxygen, and the only brands of commercial copper which do not contain any of the above constituents other than in traces, and which would therefore pass the above specification, are the various remelted electrolytic brands and native copper.

Lead.—As little as 0·1 per cent. in the absence of oxygen makes copper unworkable hot. The presence of 0·3 per cent. of arsenic renders it harmless.

Bismuth.—It has been proved that in the absence of the correct proportion of oxygen, 0·005 per cent. will make a pure electrolytic copper of inferior working properties. Such a copper might pass the American Specification as regards conductivity and analysis, but would be rejected by a bending test such as is applied in England. It has been proved conclusively that arsenic will neutralize the injurious effects of bismuth even when the latter is present in quantity of 0·05 per cent.

Tin.—Not present in commercial refined copper, but has been added to copper for tubes up to 1 per cent., for the purpose of hardening them.

Antimony.—Toughens the metal and increases the tensile strength. Traces only are found in commercial copper, but the author thinks there is a future for copper containing this metal and oxygen in suitable proportions.

Arsenic.—Usually present in what is known in England as “tough pitch” copper. It is extremely beneficial in copper for copper-smiths’ work.

Zinc.—Never present in refined copper, but sometimes added to copper for the purpose of obtaining sound castings for certain purposes.

Manganese.—Never present in refined copper, but has been used and recommended for use similar to zinc.

Nickel.—Sometimes present in refined copper; it intensifies the injurious effects of bismuth and lead. In England 1 to 2 per cent. has been added to copper for use as loco tubes and stays.

Phosphorus.—Not present in refined copper, but present to the extent of 0·6 per cent. as a rule in casting oxygen-free copper. Such metal is good quality, and can be rolled hot and drawn down.

Silicon.—Not present in refined copper, but necessary for electrolytic castings, when 2 per cent. cupro-silicon is added to the molten cathodes before casting.

Oxygen.—The most important element in copper. Present in all copper, even in metal containing 0·02 to 0·03 per cent. phosphorus.

Copper refiners are chiefly concerned with the lead, bismuth, arsenic, oxygen, and sometimes nickel. These elements may be considered as follows:—

Lead and Bismuth.—The elements which in pure copper free from oxygen render the metal brittle and lower the tensile strength, especially at high temperatures. The following results were obtained by Roberts-Austen working with a very pure copper, cast with every precaution to exclude oxygen, to which had been added 0·1 per cent. bismuth:—

Temperature, Degrees C.	Ultimate Strength, Pounds per Square Inch.	Elongation per Cent.
15	18,020	20·0
101	11,510	15·0
162	5,620	0·0
199	3,860	0·0
274	4,940	0·0
292	2,770	0·5

The author has proved that under similar conditions to the above 0·005 per cent. bismuth and similar quantities of lead in the complete absence of oxygen or arsenic will render copper unworkable hot.

Arsenic and Oxygen.—Not only toughen copper, but neutralize the injurious effects of bismuth and lead.

“It is an impossibility for any refinery to supply billets for rolling which do not contain one or other of these elements (oxygen or arsenic) in quantity sufficient to affect working properties.” Roberts-Austen added various percentages of arsenic to pure copper under similar conditions to the bismuth tests described above, and the following figures are taken from his results:—

Arsenic, per Cent.	Condition.	Temperature, Degrees C.	Ultimate Stress, Pounds per Square Inch.	Elongation per Cent.
1·2	As cast	20	24,840	20
		224	16,460	15
		346	14,860	10
1·5	As cast	15	26,460	20
		215	19,450	37
		18	30,150	30
0·2	Worked and annealed	144	30,960	21
		249	28,730	30
		18	33,420	37
0·5	Worked and annealed	258	30,030	23
		446	20,000	13

The author has proved that copper containing as much as 0·1 per cent. of bismuth can be rolled and bent in the presence of 0·6 per cent. arsenic.

F. Johnson's results are quoted as proving that oxygen neutralizes the injurious effects of bismuth.

"All refined copper, whether arsenical or non-arsenical, must of necessity contain oxygen when cast from a refining furnace as distinct from a crucible."

The superiority of arsenical copper for locomotive firebox plates has been shown by Dean and by Watson. A few results from Dean's work are as follows :—

Composition per Cent.			Mileage.
Arsenic.	Lead.	Copper.	
0·013	0·043	99·828	177,633
0·042	0·056	99·810	54,564
0·292	0·126	99·250	506,341
0·534	0·051	99·195	489,334
0·811	0·081	99·901	493,994

The following are results given by Watson :—

	Lead, per Cent.	Arsenic, per Cent.
Three good plates . . .	0·079	0·847
	0·025	0·440
	0·136	0·332
	0·332	0·192
	0·226	0·142
Eight bad plates . . .	0·124	0·049
	0·384	0·065
	0·194	0·047
	0·214	0·046
	0·164	0·053
	0·215	0·047

In refined copper there must be three times the quantity of arsenic as there is lead in order to get a good metal.

Arsenical tough copper is altogether superior to pure copper for making gun-metal and alloys of that type, and is always used for such purposes, to the author's knowledge, in some of the largest brass foundries in England.

The disadvantages of the American standard specifications are finally enumerated as follows :—

1. They do not represent the modern views of metallurgists as shown by recent researches, and are not drawn up in accordance with known facts published by practical users and makers of copper.

2. They put makers of tough copper at a great disadvantage, although modern research shows "tough" arsenical copper is more suitable for making into tubes, rods, and plates than the copper recommended.

3. The methods of rejection or acceptance of parcels of copper by the method of sampling and analysis as described by the specification are

unfair to the maker, and are against the experience of practical refiners and chemists.

4. The physical tests are quite inadequate, as they contain no reference to tensile strength, elongation, or bending tests.

5. Chemical tests are of no value unless the various impurities likely to be in copper are specified and limited.

6. Copper which is suitable for one purpose may be quite unsuitable for another purpose, therefore no one specification can cover copper for all purposes.

Gases in Aluminium.—Analyses by M. Guichard and P. R. Jourdain* show that the gases evolved when commercial aluminium is heated consist mainly of hydrogen, but the quantity is very small when the metal is uncorroded; corroded metal contains much carbon dioxide.

II.—RARE METALS.

Preparation of Ductile Tungsten.—The process described by O. Ruff† consists in reducing commercial tungsten trioxide in hydrogen to the dioxide at 1000° , and forming the oxychloride, which is distilled and transferred to hydrochloric acid, which precipitates the pure trioxide. This is washed and dried, and then ignited at 1200° , causing great shrinkage. The material is then powdered and reduced in hydrogen at 1250° to a crystalline powder, which is compressed under 5000 atmospheres, heated in hydrogen, first at 1300° with a little carbon, and then in an electric furnace at 2620 – 2650° . The rods, which have now shrunk considerably, are brittle, but are rendered malleable and ductile by hammering at 1250° in an atmosphere of hydrogen. The ductile rods are then drawn at 400 – 600° through diamond dies, the wire becoming more ductile in the process until it can be drawn cold. The metal thus obtained is silvery, does not oxidize below red heat, and resists concentrated acid, even hydrofluoric acid.

Tungsten.—The manufacture of metallic tungsten is described by G. Erhard.‡ The sodium tungstate prepared by fusion of the ore with sodium carbonate is recrystallized, and is then decomposed by hydrochloric acid with the addition of 6 per cent. of nitric acid, which is added after the hydrochloric acid has been raised to boiling. The precipitate is washed and dried, and is then mixed with the reducing agent in the proportions 100 parts tungstic acid, 14.1 parts wood charcoal, and 2 parts resin. The metal contains 92–94 per cent. of tungsten, and is then ground in a flint-mill lined with hard porcelain, and washed in running water, after which the content of metal rises to 96.5 per cent.

* *Comptes Rendus*, 1912, vol. clv. p. 160.

† *Zeitschrift für angewandte Chemie*, 1912, vol. xxv. p. 1889.

‡ *Metallurgie*, 1912, vol. ix. p. 441.

III.—ALLOYS.

Alloys of Copper, Zinc, and Aluminium.—The alloys of this series richest in copper have been investigated by H. C. H. Carpenter and C. A. Edwards.* There is no ternary compound or ternary eutectic in this part of the system, although a ternary eutectic point may exist near to the aluminium-zinc line. The most important part of the liquidus surface consists of two areas, corresponding with the solidification of α and β solid solutions respectively. These areas include all those alloys which have a yellow colour, and this part of the system has been investigated down to 400° . The α alloys do not undergo any transformation during cooling, but remain homogeneous, and the corresponding area increases with falling temperature—that is, the solubility of zinc and aluminium in copper increases with falling temperature. The β alloys, however, are resolved into α and γ on cooling. The eutectoid points in the two binary systems are connected by a curve which falls from 570° on the aluminium side to 470° on the zinc side, the intensity of the recalescence gradually diminishing in the same direction. A thermal change at 700° is also observed, being strongest in the alloys approaching the eutectic proportion, and perhaps indicating a polymorphic transformation of the β phase. The microscopical observations are in agreement with these results. The bearing of the results on the industrial aluminium brasses is also considered.

Alloys of Iron and Zinc.—Measurements of the electromotive force of these alloys by E. Vigouroux, F. Ducelliez, and A. Bourbon† indicate the existence of four definite compounds, FeZn_7 , FeZn_3 , Fe_3Zn , and Fe_5Zn , of which only the first two have been previously recognized.

Alloys of Lead, Bismuth, Tin, and Cadmium.—The first metallographic study of a quaternary system of alloys is due to N. Parravano and G. Sirovich,‡ and deals with the fusible metal series. The system has been examined very fully, the results being exhibited in the form of projections of a tetrahedral model. It is not likely that any compounds are formed, and the observations indicate that any solid solutions are practically resolved into their components before the quaternary eutectic point is reached, so that the phases then present are the four pure metals. The most fusible alloy of the series contains 10.10 per cent. cadmium, 13.13 per cent. tin, 27.27 per cent. lead, and 49.50 per cent. bismuth. This composition differs considerably from that assigned to the quaternary eutectic by Guthrie, whose alloy is shown to contain crystals of primary bismuth.

Alloys of Silver, Tin, and Lead.—These ternary alloys have been studied by N. Parravano§ in connection with the general theory of

* *Internationale Zeitschrift für Metallographie*, 1912, vol. ii. p. 210.

† *Bulletin de la Société chimique*, 1912 [iv.], vol. xi. p. 480.

‡ *Gazetta chimica italiana*, 1912, vol. xlii. 1, p. 630.

§ *Internationale Zeitschrift für Metallographie*, 1912, vol. iii. p. 15.

ternary systems. This is a case in which two of the binary systems form simple eutectiferous series, whilst in the third a compound occurs, formed during cooling by a reaction occurring between one component and the liquid. The method of theoretical treatment employed is that of the thermodynamic potential.

Aluminium Solder.—The following composition for an aluminium solder has been patented by R. J. Busch *: 0.25 per cent. vanadium, 9 per cent. bismuth, 15.5 per cent. aluminium, 7 per cent. antimony, 2.25 per cent. magnesium, 66 per cent. tin. The vanadium is melted first, and the other ingredients added in the order above mentioned.

Aluminium-Platinum Alloys.—A thermal analysis of these alloys by M. Schubigin † shows that a single compound, Al_3Pt , is formed, and causes a break in the freezing point curve at 787° . The same compound is obtained by the action of hydrochloric acid on alloys containing more aluminium than corresponds with this formula. Between 70 and 90 per cent. of platinum a second compound appears, of yellow colour and unattacked by ferric chloride, which etches the compound Al_3Pt . These rich alloys are very brittle, and leave a residue of variable composition when attacked by acids.

Cadmium and Tin Alloys.—A reinvestigation of cadmium-tin alloys by A. P. Schleicher ‡ fixes the eutectic point at 177° and 67.6 atomic per cent. of tin. γ -tin holds a considerable quantity of cadmium in solid solution, but this is chiefly given up at 127° on cooling, when γ -tin changes into β -tin, which has a much smaller solubility for cadmium. A compound is not formed.

These results are discussed by W. Guertler,§ who shows that as such reactions in the solid state do not attain completion during cooling, it is not possible to infer directly the composition of the solid phase from the maximum of the thermal effect. The decomposition of a solid phase is usually complete during cooling, although undercooling may occur, but the formation of a new phase from two solid phases may remain very incomplete, especially if the grain of the alloy is coarse. The conditions of the change are most favourable when the reacting substances are present as the decomposition products of a previous reaction. It is shown that the resolution of the solid solution of cadmium in γ -tin leads to a constituent closely resembling the troostite in hardened steels, and consisting in a similar manner of a finely-divided mixture of two solid phases.

It is also shown that in order to obtain the true value of the "eutectic times" the velocity of cooling must be taken into account, and this may be determined graphically from the cooling curves.

* *Metallurgical and Chemical Engineering*, No. 5, May 1912, vol. x. p. 309.

† *Comptes Rendus*, 1912, vol. clv. p. 156.

‡ *Internationale Zeitschrift für Metallographie*, 1912, vol. ii. p. 76.

§ *Ibid.*, p. 90.

Bearing-Metal Alloys.—An investigation into the effect of repeated melting, heating and cooling of bearing-metals on their composition and mechanical properties has been carried out at the Royal Laboratory at Gross-Lichterfelde-Weste.* The results show that repeated melting does not substantially affect the composition of white metal, and that its mechanical strength is favourably affected by rapid cooling and adversely by slow, the latter metal being about 10 per cent. weaker.

Cerium-Aluminium Alloys.—Cerium alloys with aluminium, according to R. Vogel,† with the development of much heat. Porcelain vessels can be used for all the alloys, except those richest in aluminium, which are melted in carbon tubes. The two metals mix with difficulty, and repeated remelting is necessary to obtain homogeneous alloys.

The diagram of equilibrium shows that five compounds are formed, of which one, CeAl_3 , has the remarkably high melting point of 1450° . The compound Ce_3Al also forms a maximum on the freezing point curve at 614° , whilst the remaining three compounds, Ce_2Al , CeAl , and CeAl_4 , are indicated by breaks in the curve at 595° , 780° , and 1250° respectively. The last compound also has a transformation point at 1005° . Solid solutions are not found to any appreciable extent.

The alloys, if free from carbon, are stable towards air and water, with the exception of those very rich in cerium, which oxidize in air, but if carbon is present they readily disintegrate.

The hardness is a maximum for the compound CeAl_2 , which has $H=6$. This compound is unattacked even by concentrated mineral acids. The most definite crystals are those of CeAl . Only the alloys containing a high percentage of cerium give sparks when filed.

Cobalt and Carbon.—The system of cobalt-carbon has been investigated by G. Boecker,‡ who finds that pure cobalt melts at 1448° . At about 1700° it is capable of dissolving 3.9 per cent. of carbon, which separates almost entirely as graphite on slow cooling. The eutectic point is at 1300° and 2.8 per cent. of carbon, and at this temperature cobalt retains 0.82 per cent. of carbon in solid solution. As the temperature falls the solubility of carbon in solid cobalt diminishes, reaching about 0.3 per cent. at 1000° . The general form of the curve thus resembles closely that of the iron-carbon system. A cobalt carbide has not been detected. The microsections show a well-developed eutectic structure, having as components graphite and the solid solution.

The total carbon in the alloys is best estimated by the chromic acid process, using very fine borings, and a larger quantity of chromic acid than is required for the ordinary analysis of iron.

Distillation of Binary Metal Mixtures.—The separation of an intermetallic compound from excess of the second metal in a binary alloy

* *Engineer*, vol. cxiii. p. 433.

† *Zeitschrift für anorganische Chemie*, 1912, vol. lxxv. p. 41.

‡ *Metallurgie*, 1912, vol. ix. p. 296.

is discussed.* The isolation of the compound is most likely to be successfully effected when its tension of dissociation is very low at the temperature of volatilization of the second metal; also, the vapour pressure of the second more volatile metal should fall abruptly when it is in a state of combination in the compound. The intermetallic compound should not form solid solutions with either of its constituents. The Mg-Zn series and the compound MgZn_2 are cited as a case in point.

The author obtained inconclusive results on attempting to separate compounds mutually soluble in their constituent metals. A quantitative separation of copper from cadmium was effected by distillation *in vacuo*.

German Silver.—A description of the manufacture of German silver and similar alloys by H. Kloss,† states that the German practice is to place alternate layers of copper, zinc, and nickel in the crucible, to cover with charcoal, and to melt as rapidly as possible. Only a third of the zinc and nickel is added in this way, the remainder being added after the whole is fluid. Stirring is commonly performed by means of an iron rod, but this is undesirable, and a carbon rod should be used. Iron rods may, however, be protected by a coating of borax and fireclay. In the English method, the copper is melted in two separate portions, being alloyed in one case with zinc, and in the other with nickel. The copper-zinc alloy is cast into thin plates, broken up whilst red-hot, and added to the molten copper-nickel alloy. In a more recent method, a mixture of 3.75 parts of copper, 0.25 parts of zinc, and 1.5 parts of nickel is introduced into a red-hot crucible, and melted rapidly under charcoal, and the remainder of the metal is then added in the form of very small fragments. German silver may be soldered with metal of the same composition if a blowpipe is used, or solders may be made of the following composition:—

	Soft.	Medium.	Hard.
Copper	4.5	35.0	40
Zinc	7.0	56.5	50
Nickel	1.0	9.5	14

Gold and Silver.—A new investigation of the alloys of gold and silver, by U. Raydt,‡ confirms earlier results. The crystallization interval is small, and the alloys are consequently nearly homogeneous.

Lead, Tin, and Antimony.—A new investigation of these alloys, by W. Campbell,§ confirms the author's previous results. The lower

* *Engineering*, October 25, 1912, vol. xciv. p. 583.

† *Giesserei-Zeitung*, 1912, vol. ix. pp. 347, 410.

‡ *Zeitschrift für anorganische Chemie*, 1912, vol. lxxv. p. 58.

§ *Metallurgie*, 1912, vol. ix. p. 422.

ternary point is found to lie at 40 per cent. lead, 2.5 per cent. antimony, and 57.5 per cent. tin, whilst Loebe found 36.5 per cent. of lead and 60.5 per cent. of tin. In other respects the two authors are in accord. Many photomicrographs are given, illustrating the structure of these alloys, which often differs from that to be expected from the equilibrium diagram, owing to the slowness of reaction between solid components.

Light Aluminium Alloys.—A partial study of the light alloys of aluminium with copper and zinc has been made by M. Levi-Malvano and M. Marantonio.* Alloys containing 2 per cent. copper and 10 or 20 per cent. zinc are completely homogeneous, but alloys containing 6.8 or 10 per cent. copper and 10 or 4 per cent. zinc contain two distinct constituents. A eutectic structure appears only in the alloys very rich in zinc. The study is incomplete, and the properties of the alloys have not been examined in detail.

Nickel-Cobalt Alloys.—These alloys have been reinvestigated by R. Ruer and K. Kaneko.† The freezing point curve, as previously determined by Guertler and Tammann, lies smoothly between the two end-points (nickel 1451° and cobalt 1491°). The curve of disappearance of magnetism on heating is continuous, and is convex upwards, from 360° for nickel to 1102° for cobalt. The temperature range within which the transformation takes place is very small. It has not been found possible to retain the alloys in the non-magnetic state by quenching.

All the alloys show a polygonal structure when etched with ferric chloride. Pure cobalt and alloys rich in cobalt show well-marked striation due to twinning, which is absent from the nickel end of the series. Nickel oxide is soluble in nickel, and forms a eutectic closely resembling that of copper and copper oxide.

Non-Corrosive Alloys.—An alloy containing 92 per cent. aluminium, 5 per cent. copper, 2 per cent. bismuth, and 1 per cent. silicon has been patented‡ as resisting the corrosive action of sulphuric acid better than other light alloys of aluminium, and consequently being especially suitable for use in mines.

Production of Porous Metals.—The fact that the eutectic alloy has the lowest melting point of all the alloys of a binary system has been made use of by H. I. Hannover§ for the production of porous plates for storage batteries, &c. Taking, for example, the system lead-antimony, the eutectic composition is lead 87 per cent., antimony 13 per cent., and we may consider that all other alloys of the system are composed of this eutectic and either lead or antimony. If a solid plate

* *Gazzetta chimica italiana*, 1912, vol. xlii., 1, p. 353.

† *Metallurgie*, 1912, vol. ix. p. 419.

‡ *Engineer*, June 1912, vol. cxiii. p. 651.

§ *Metallurgical and Chemical Engineering*, No. 9, September 1912, vol. x. p. 509.

of such an alloy be heated, the veins of eutectic will melt first, and by suitable means, such as centrifuging, may be almost completely separated, leaving a porous mass of lead or antimony as the case may be. By this means, using an alloy containing 96 per cent. of lead and 4 per cent. of antimony, the author has succeeded in obtaining lead accumulator plates, which, on testing, were found to possess 4-4.5 times the capacity of ordinary lead plates of the same weight.

Photomicrographs illustrating the process are shown.

Radium Alloys.—In an experiment by F. de Mare and C. Jacobs,* a mixture of radium sulphate, calcium carbonate, silver chloride, and carbon was heated in a furnace. A yellowish-white alloy of silver and radium was obtained. In another experiment, a solution of radium acetate was electrolyzed between platinum electrodes, and a brown, active deposit was obtained.

Structure of Eutectics.—It is shown by R. Vogel† that the crystallization of eutectics follows the same course as that of pure substances. The two components crystallize simultaneously, and not alternately. Growth takes place perpendicularly to the cooling surface, or radially from centres of crystallization. The normal arrangement of a eutectic is therefore the spherulitic. There are two possible cases. The power of spontaneous crystallization and the linear velocity of crystallization both increase as the undercooling becomes greater, but either the one or the other may increase more rapidly. If the curve of spontaneous crystallizing power rises the more rapidly, quick cooling makes the eutectic more coarse-grained, whilst if the linear velocity of crystallization increases the more rapidly, quick cooling produces a finer grain. It is shown that both cases actually occur. The eutectic of zinc and cadmium shows the first effect well. Ordinary slow cooling produces a fine-grained spherulitic structure, whilst rapid cooling, by plunging the lower part of an iron crucible in water, produces a coarse structure, in which the two components are arranged in nearly parallel rods perpendicular to the cooled surface.

The fact that in most eutectics one compound appears to enclose the other is also explained by a consideration of the relative velocities of crystallization, a difference in this respect causing the liquid at the boundary to be differently undercooled with respect to the two components.

Structure of Ternary Alloys.—It has been observed by G. H. Gulliver‡ that ternary alloys frequently show two kinds of primary crystals in contact with a ternary eutectic, instead of the single type of primary crystals accompanied by a binary and a ternary eutectic, assumed by the ordinary theory of solidification. The effect is attributed to segregation during cooling. Thus in an alloy of bismuth, tin, and lead,

* *Bulletin de l'Académie royale de Belgique*, 1912, p. 53.

† *Zeitschrift für anorganische Chemie*, 1912, vol. lxxvi. p. 425.

‡ *Proceedings of the Royal Society of Edinburgh*, 1912, vol. xxxii. p. 36.

the primary crystals of bismuth attract to themselves the bismuth of the binary eutectic, whilst the tin particles also migrate and form skeleton crystals. Similarly, some alloys of copper, antimony, and lead show two kinds of primary crystals, namely, antimony and copper antimonide.

Thallium and Tellurium Alloys.—A thermal study of these alloys by M. Chikashigé* shows that two compounds are formed, Te_2Tl_3 and TeTl , of which the first is brittle and melts at 428° , and forms solid solutions with thallium. It reacts with the liquid at 305°C. to form the second compound, which does not enter into solid solution. The eutectic point $\text{TeTl}-\text{Te}$ lies at 200° . Between 100 and 76 per cent. Tl two liquid layers are formed.

IV.—PHYSICAL PROPERTIES.

Aachen Technical School—Work of the Metallurgical Department.—The work of this institution during the last ten years is summarized by W. Borchers.† The researches carried out include many on the smelting of the non-ferrous metals, and the conditions of roasting of the corresponding sulphide ores and mattes. The attempts to utilize aluminium silicates in the manufacture of aluminium gave promising results, but interest in this subject is declining, as the present supply of bauxite appears to be sufficient. Much work has, however, been done on the corrosion of commercial aluminium vessels. It is found that the absolute quantity of iron and silicon in the metal is of less importance than the ratio of the two. If the silicon present is insufficient to combine with all the iron as FeSi_2 , iron favours corrosion. The influence of rarer metals, especially cerium, on the resistance of aluminium to corrosion has also been studied. Another important series of experiments, not yet completed, has resulted in the production of alloys which are more resistant to chemical reagents than even the noble metals.

Action of Mercury Salts on Aluminium.—The well-known action of mercury salts on aluminium, according to P. Nicolardot,‡ is very strongly marked when the metal is pure, action being perceptible in solutions containing less than 0.001 per cent. of mercuric chloride. If aluminium foil is painted with a 0.1 per cent. solution of mercuric chloride, the white filaments of alumina are produced. Aluminium containing 3 per cent. of copper is not effected.

Changes of Density due to Pressure.—Very careful determinations of density have been made by J. Johnston§ and L. H. Adams,

* *Zeitschrift für anorganische Chemie*, 1912, vol. lxxviii. p. 68.

† *Metallurgie*, 1912, vol. ix. p. 601.

‡ *Bulletin de la Société chimique*, 1912 [iv.], vol. xi. p. 410.

§ *Journal of the American Chemical Society*, 1912, vol. xxxiv. p. 563; *Zeitschrift für anorganische Chemie*, 1912, vol. lxxvi.

using an improved form of pycnometer, and it is shown that the density of homogeneous substances is not changed by powdering them. It is also found that bismuth, formed into wire by forcing through a hole 1 mm. diameter, has a density 9.7692 at 25° (corrected to vacuum), and that this becomes 9.7767 on annealing at 230°. The change of density is therefore in the same direction as for other metals, contrary to the well-known result of Spring. The method of density determinations is not a good one for the study of chemical change in solids, owing to the difficulty of ensuring homogeneity.

Chemical Resistance of Metals.—In a lecture on this subject W. J. Müller* dwells on the importance of electro-chemical phenomena in governing the attack on metals by reagents and corrosive liquids. The chemistry of passivity and of rusting is also discussed.

Cleavage Planes in Metals.—A hypothetical explanation of cleavage planes in metals is proposed by J. Stark.† The valency electrons are held to be responsible for the electrical conductivity of the metal, and also for the cohesion. "Electrical cleavage planes," along which electrons may be moved by an infinitely small electrical force, are stated to be identical with the mechanical cleavage planes. In a mass of metal made up of crystal grains, the resistance to shearing is proportional to the area of the bounding surfaces in unit volume, and therefore increases with increasing fineness of grain of the metal. Quenching or cold-working favours a fine grain, and thus raises the resistance—that is, the elastic limit. According to this hypothesis, isolated crystals of non-metallic substances should offer a greater resistance to shearing than similar crystals of metals.

Cold-Working of Metals.—In an important lecture on this subject, G. Tammann‡ states his views as to the nature of the hardening of metals by cold-working. The hypothesis of an amorphous modification is rejected, on the grounds that it involves a violation of the phase rule, and also because it does not account for the difference between the action of uniform (hydrostatic) pressure, and of pressure causing flow. Further, the effect of pressure should be to favour that modification which has the smaller volume, whilst cold-working actually produces a diminution, and not an increase, of density. The hardening is explained by the formation of an increasing number of crystalline lamellæ, without any destruction of the true crystalline arrangement. Energy is absorbed in the formation of so many new bounding surfaces, and this reappears in the hardened metal, in the form of increased solution pressure, &c.

The recrystallization of cold-worked metals when heated is then due to surface tension, the bounding surfaces tending to become a minimum. A worked metal differs from an unworked in having its crystals definitely oriented, owing to the development of cleavage lamellæ and twinning.

* *Zeitschrift für angewandte Chemie*, 1912, vol. xxv. p. 1217.

† *Physikalische Zeitschrift*, 1912, vol. xiii. p. 585.

‡ *Zeitschrift für Elektrochemie*, 1912, vol. xviii. p. 584.

The "inoculation" of hardened metal by contact with the crystalline metal in Cohen's experiments is attributed to mechanical causes. The lowered density of the worked metal is due to the production of internal clefts and cracks as the lamellæ slip over one another. The increased elasticity and heat content of eutectics as compared with their components is explained by the fineness of their lamellæ. The lowered electrical conductivity of worked metals is attributed partly to the internal cracks, partly to orientation, it being assumed that the conductivity of a crystalline metal is greater perpendicular to the principal cleavage than parallel with it. Some experiments on drawn and twisted wires are quoted in support of this.

In the discussion, it was pointed out by G. Quincke that he had proposed a theory of the formation of thin lamellæ, and of recrystallization under the influence of surface tension, forty-four years ago. He has since modified it by his theory of the foam-structure of cast metals.

Cold-Working of Zinc.—The effect of work on cast zinc has been examined by G. Timoféef.* The metal is etched by means of a very dilute mixture of nitric and chromic acids. The crystals in the ingot exhibit numerous twinning planes. A very confused structure is obtained on compression, the pressure being applied slowly and the specimen cooled by ice. Spontaneous recrystallization begins in a few days at the ordinary temperature, whilst at 100° recrystallization is visible in a few minutes. At 300° a very coarse structure may be obtained. Twinning is readily produced by a slight shock, and local deformation by a needle, followed by annealing at 300°, gives an interesting local recrystallization.

Colouring of Metals.—In an article by G. Strahl† an account is given of the methods employed in the superficial colouring of metallic objects, most of which depend on the formation of an oxidized layer. Acids, oxidizing solutions, or heat are used, but the electrolytic deposition of a layer of oxide is one of the most general means. The anodic oxidation of a lead salt gives a coloured layer of lead peroxide, and it is found that this layer adheres best if a layer of metallic lead is first deposited on the metal to be coloured.

Condensation of Metallic Vapours.—Experiments have been made by V. Kohlschütter and C. Ehlers‡ to determine the nature of the deposits obtained by condensing metallic vapours. The metals were heated in a glass or silica tube, and the vapours condensed on a smooth plane surface of glass or silica. The distribution of the condensed particles is usually very regular, and it appears that the particles first deposited serve as nuclei for further deposition. Very often particles much larger than the average are found, and in such cases they are sur-

* *Comptes Rendus*, 1912, vol. clv. p. 430.

† *Elektrochemische Zeitschrift*, 1912, vol. xix. p. 26.

‡ *Zeitschrift für Elektrochemie*, 1912, vol. xviii. p. 373.

rounded by a clear area. The fineness of division increases with the pressure of the inert gas used. For different gases, this influence in disintegrating the metal is greater the denser the gas. This is explained as occurring by the diminution of the free path, the distribution of the particles being due to the same conditions as the Brownian movement.

Conductivity of Alloys of Copper and Arsenic.—The addition of arsenic to copper, according to N. A. Pushin and E. G. Dishler,* rapidly lowers the electrical conductivity. At 6 per cent. of arsenic the curve changes its direction, the lowering of conductivity becoming less rapid. The break indicates the limit of formation of solid solutions. The next break is at 28.2 per cent., corresponding with the compound Cu_3As . From this point the conductivity slowly increases up 42 per cent. of arsenic. It has not been found possible to prepare richer alloys owing to volatilization.

Conductivity of Liquid Alloys.—Further researches by K. Bornemann and G. von Rauschenplat† deal with two complete series, copper-nickel and copper-antimony, and several partial series. By the use of magnesia tubes the measurements have been carried above 1500° . The capacity of the tube is determined at each temperature by experiments with liquid tin. In the case of metals which react with carbon so that carbon electrodes cannot be used, it has been found best to use electrodes of copper cooled internally by water. The secondary electrodes for potential measurement are similarly constructed, and are provided with special means of maintaining a constant flow of water. A carbon tube furnace is used for heating.

Attempts to dispense with electrodes by constructing an induction furnace and calculating the conductivity proved unsuccessful, a number of factors being involved which cannot be satisfactorily determined.

The results show that whether the addition of a second metal to a molten metal raises or lowers the conductivity does not depend on whether the added constituent is a better or a worse conductor. If the second metal has a strong tendency to form a compound with the first, the conductivity is lowered by the addition of a small quantity, whilst in the absence of such a tendency, either raising or lowering of the conductivity may take place. The complete conductivity curve of copper-nickel alloys has a minimum without any sharp break, whilst that of the copper-antimony alloys has a more sharply defined minimum near the composition Cu_3Sb . This relation comes out more clearly in the temperature-coefficient curves. The minimum at Cu_3Sb is very sharp, whilst the copper-nickel curve is smooth. Some alloys of this series have a negative temperature-coefficient, either throughout the range or at low temperatures only. This is explained by increasing dissociation of the compound.

* *Journal of the Russian Physico-Chemical Society*, 1912, vol. xlv. p. 125.

† *Metallurgie*, 1912, vol. ix. pp. 474, 505.

Crystallization in Metals.—A paper by G. Tammann* discusses the influence of surface-tension on the formation of rounded crystallites in metals. If the strength f is less than the surface tension α at any temperature, the crystal face in question becomes curved, and when all the faces of a metallic crystal have reached this state the crystal assumes a spheroidal form. In a two-component system, if the freezing point curve passes through the temperature at which $f=2\alpha$, rounded crystallites will be formed above that temperature, and polyhedral crystals below. The large number of rounded forms actually observed in alloys is considered to show that such a condition is often realized. Calculations are also given to determine the conditions when the crystal is composed of thin lamellæ. Not only the absolute value of α , but also its temperature-coefficient, may be altered by increasing the number of lamellæ per unit of thickness.

The recrystallization of metals at high temperatures is attributed to surface-tension effects, the strength of the metal diminishing with increasing temperature. The facility with which worked metals recrystallize on heating is explained by the increase in the number of cleavage surfaces produced by the process of working. It is not regarded as similar to the growth of large crystals at the expense of small in a saturated solution, the latter effect being attributed to oscillating changes of temperature.

Experiments by H. Schottky,† performed in order to test the conclusions of Tammann, just described, supplement the work of Beilby and of Turner on the effect of heat on thin films of metal. Gold leaf shows a considerable contraction at 340° . Silver leaf ultimately falls to powder, the temperature at which this occurs rising with increasing thickness of the leaf. Copper in a reducing atmosphere resembles silver, whilst aluminium is practically unchanged.

The importance of the change in gold is explained by the readiness with which that metal forms cleavage planes, so that when a temperature is reached at which the surface-tension gains the upper hand, contraction can take place without producing an actual rupture of the metal, whilst silver is torn in the process. Oxygen influences silver by dissolving in the metal, and so either lowering the strength or increasing the surface-tension.

Experiments on the tensile strength of silver foil at high temperatures show that the strength per unit area diminishes with decreasing thickness of the foil, and with increasing temperature. A calculation is made involving certain assumptions, but tending to show that the surface-tension forces are sufficient in magnitude to bring about the recrystallization observed in metals at high temperatures.

Crystallization of Worked Metals.—Measurements have been made by F. Robin‡ of the size of grain of several metals after cold-rolling and annealing at various temperatures. The effect of impurities

* *Nachrichten der k. Gesellschaft der Wissenschaften zu Göttingen*, 1912.

† *Ibid.*

‡ *Comptes Rendus*, 1912, vol. clv. p. 585.

is to diminish the size of grain obtained on annealing without affecting the temperature at which annealing sets in.

Disintegration of Aluminium Articles.—In a discussion of this subject G. Goldberg* states that the disintegration of aluminium articles in stock, before having been used, has attracted the serious attention of manufacturers. The investigation of the subject at Gross-Lichterfelde has shown that neither silicon nor nitrogen plays any important part in the action. The crust and blisters found consist almost entirely of alumina. Changes of temperature are without influence. Tap water has a much greater corrosive influence than distilled water, especially as regards irregular and local pitting. The action in such cases is electrolytic, and depends mainly on differences of potential between unequally hard portions of the aluminium. Cold work should therefore be carefully removed by heating to 400°–450°, and slowly cooling.

Disintegration of Metals by Heat.—Experiments by G. Reboul and E. G. de Bollement† show that if two sheets of dissimilar metals are placed in a tubular electric resistance furnace, and arranged facing one another, at only a short distance (1–2 mm.) apart, on raising the temperature a deposit of one metal is formed upon the other. On heating strips of copper and platinum foil together thus, a dark deposit was obtained on the platinum. On raising the temperature still higher, or on prolonging the heating, the deposit disappeared. The copper was cut in the shape of a cross when the deposit also was cruciform. On repeating the experiment with the same piece of copper, the deposit obtained was much less dense. The deposit consisted of copper metal or of a copper compound.

The phenomenon was observed to take place equally well in air at ordinary pressure, *in vacuo*, and in atmospheres of oxygen, nitrogen, and carbon dioxide. When hydrogen was employed a modified form of deposit was obtained. Other metals were successfully substituted for both the copper and the platinum foil, but, whilst copper and silver gave particularly good deposits, attempts to obtain deposits from iron, nickel, and aluminium failed.

It is concluded that the effect is due to occluded gases in the metal which expand on heating, producing a number of minute explosions, whereby particles of the metal are torn away and deposited on neighbouring surfaces.

J. H. G. Robertson, discussing similar effects,‡ arrives at the conclusion that occluded gases do not carry metallic particles with them when liberated, nor can the phenomenon be entirely due to volatilization. It is suggested that the deposit may be an oxide of the metal which is more volatile than the metal itself. Experiments with platinum heated in an atmosphere of oxygen are described in support of this theory.

* *Giesserei-Zeitung*, 1912, vol. ix. p. 534.

† *Engineering*, October 25, 1912, vol. xciv. p. 577.

‡ *Nature*, August 29, 1912.

Yet another explanation may be found by consideration of the cathode volatilization of metals.

Duration of Sound in Alloys.—F. Robin* gives the results of experiments to determine the effect of temperature on the duration of sound in alloys. The test-bars were suspended by a light, flexible wire, and the duration of the sound, after the bars were struck a standard blow, was determined for different temperatures. For pure metals the duration decreases regularly with rise of temperature. The alloys of copper and nickel show a change at 100°C. , and all copper-nickel alloys and German silver show a sudden rise at 320°C. , indicating a transformation at this temperature. The temperature at which the sound ceases varies in metals and alloys, and in some cases this corresponds with the fall in hardness.

Effect of Vibration on Electrical Resistance.—Some experiments with wires by H. L. Brakel† show that when a wire is subjected to regular mechanical vibrations its electrical resistance is increased to an extent which increases at first rapidly with the number of vibrations, and then approaches a constant value. The effect on nickel is much less at higher temperatures, whilst nichrome is affected in the opposite manner. The change due to vibration is always removed by annealing at a red heat. With large amplitudes a much greater number of vibrations is necessary before a constant value is approached.

Electrical Conductivity of Alloys.—In a lecture to the Bunsen Society, W. Guertler‡ describes the methods of studying the constitution of alloys by means of their conductivity, and a comparison is made with the method of thermal analysis. The following modes of procedure are available:

1. Specimens of known composition are taken, and their resistance is determined at a number of different temperatures, so giving resistance-temperature curves. It is not necessary that the specimens should be of known dimensions. The curves are then used in the same way as cooling curves in thermal analysis.

2. If the specimens are capable of being worked to definite dimensions, their resistances at a single temperature are compared, giving composition-resistance curves.

Modifications of these methods are also described, by means of which the areas in the equilibrium diagram may be mapped out.

A paper on this subject by N. J. Stepanoff§ describes the method of casting suitable rods of alloys by drawing the molten alloy by means of a pump into glass or porcelain tubes coated internally with lamp-black. The method of measurement used is that of the potential drop, the four contacts being made by means of spring clamps.

* *Revue de Métallurgie*, 1912, vol. vi. pp. 618-637.

† *Physical Review*, 1912, vol. xxxv. p. 185.

‡ *Zeitschrift für Elektrochemie*, 1912, vol. xviii. p. 601.

§ *Zeitschrift für anorganische Chemie*, 1912, vol. lxxviii. p. 1.

The alloys of magnesium with lead, tin, copper, zinc, and bismuth, are then examined in succession, and the curves of conductivity and temperature-coefficient are drawn. The only typical curve for alloys containing a single compound without any solid solutions is that of magnesium and bismuth. In the other cases solid solutions are formed to a small extent. Magnesium and copper form a series which well illustrates the influence of more than one intermetallic compound in a series.

Lastly, by the comparison of a number of data, it is shown that the temperature-coefficient of the resistance has nearly the same value for most intermetallic compounds, and is always much greater than that of a solid solution.

Electrical Properties of Copper-Tin Alloys.—According to R. Ledoux,* the electrical resistance of the copper-tin alloys gives a curve which has a sharp cusp at the composition of the compound Cu_3Sn , and an equally pronounced minimum at Cu_3Sn . There is no other distinct point on the curve. The thermo-electric power has a maximum value for Cu_3Sn , and a minimum for Cu_4Sn . The curve of variation of thermo-electric power with temperature has a much more distinct cusp at Cu_3Sn . The specimens must be annealed for a considerable time below their lowest point of transformation. The absence of any point corresponding with the compound CuSn is perhaps accounted for by insufficient annealing.

Electrical Properties of Copper-Zinc Alloys.—The conductivity curve of the alloys of copper and zinc, as determined by L. Norsa,† shows a sharp cusp corresponding with the compound CuZn , with a minimum at about Cu_2Zn_3 , the other discontinuities being less well marked. The temperature-coefficient curve has an additional cusp at CuZn_3 , as has the curve of thermo-electric power. The point Cu_2Zn_3 , although not mentioned by the author, is distinctly marked on each of the curves.

The Electron Atmospheres of Metals.—Some remarkable experiments by R. W. Wood‡ indicate that an atmosphere of electrons is attached to metallic surfaces. Thin silver films may be cut through in a number of places by a diamond point without greatly lowering the electrical conductivity. Two plates of polished speculum metal, separated by two quartz fibres about five wave-lengths in diameter, allow a current of several milliamperes with an applied potential of one volt. Separation by means of finely powdered quartz gives similar results.

Expansion of Alloys of Aluminium and Zinc.—Some measurements of expansion by W. Smirnoff§ show that the coefficient of

* *Comptes Rendus*, 1912, vol. clv. p. 35.

† *Ibid.*, p. 348.

‡ *Philosophical Magazine*, 1912 [vi.], vol. xxiv. p. 316.

§ *Comptes Rendus*, 1912, vol. clv. p. 351.

expansion of alloys of aluminium and zinc is a maximum for the alloy with about 32 per cent. of zinc, and then falls to a minimum corresponding with the compound Al_2Zn_3 . There is a second maximum near the zinc end of the series. All alloys which contain the compound Al_2Zn_3 undergo a transformation, indicated by expansion, at $260^\circ\text{--}270^\circ$.

Flow of Metals.—The view has been propounded by J. Johnston * that the flow of metals under differential pressure is due to an actual melting, the melting point being lowered by pressure. It is well known that the melting point of most substances is raised by pressure, but Poynting has shown that, if the liquid phase is free to escape, so that the pressure acts only on the solid phase, the melting point is always greatly lowered, whether the substance expands or contracts on melting. A thermodynamical calculation leads to the result that the pressure in atmospheres, ϕ , necessary to melt a substance at the absolute temperature θ is:

$$\phi = 95.1 Q_1 D_1 \log \frac{T_1}{\theta}$$

where T is the absolute melting point, D the density at the melting point, and Q the heat of fusion per gramme.

In the following table the values of ϕ necessary to produce melting at 27° (300° absolute) are given:

	T_1	Q	ϕ_{27}
Potassium	335	15.7	64
Sodium	370	31.7	266
Lead	600	5.4	1,760
Tin	505	14.1	2,200
Bismuth	543	12.5	3,000
Cadmium	594	13.7	3,300
Aluminium	931	42.0	5,100
Zinc	692	28.0	6,900
Silver	1233	23.0	14,000
Copper	1356	43.0	24,000
Palladium	1823	36.3	31,000
Platinum	2028	27.2	46,000

This is in accordance with the tendency to flow, which is actually observed, this being in diminishing order: Potassium, sodium, lead, thallium, tin, bismuth, cadmium, zinc, antimony. It is found that the same order in the table represents that of decreasing compressibility and of increasing elasticity. It is therefore suggested that the flow of metals is due to an actual melting, very high pressures being reached locally, even when the pressure as a whole is low. The molten material then flows into the interstitial spaces and immediately recrystallizes, until the further repetition of the process becomes impossible, and the "upper elastic limit" is reached. When the rate of recrystallization is

* *Journal of the American Chemical Society*, 1912, vol. xxxiv. p. 788.

very rapid, the structure may be very minute, and Beilby's "amorphous" material results.

It is further suggested that the melting point and other related properties are really functions of the "molecular vibration frequency," a characteristic quantity which has been studied lately by several physicists.

Hair Silver.—The fine spicular modification of silver known as "hair silver" has been investigated by V. Kohlschütter and E. Eydmann.* It may be obtained by heating solid silver sulphide without solution or fusion. It is best obtained by heating the sulphide in hydrogen at 360°, afterwards raising the temperature to 450°. Simple dissociation plays a part, as hair silver may even be obtained by heating the sulphide in a vacuum or in carbon dioxide. The only other silver compound which yields hair silver is the selenide. The authors explain the reaction by the assumption of a considerable vapour pressure of these compounds at low temperatures.

The Influence of Gases on Conductivity.—According to A. Sieverts,† the electrical conductivity of wires of platinum, copper, nickel, and iron is hardly affected by the absorption of hydrogen at atmospheric pressure between 20° and 920°. The conductivity of a silver wire is diminished by heating in hydrogen, but this is not due to absorption, as the conductivity does not return after heating in a vacuum or in oxygen. Nickel is not affected by carbon monoxide at 1000°. The conductivity of palladium is diminished by hydrogen, the change being proportional to the concentration of the absorbed hydrogen. The results in general confirm the view that palladium containing hydrogen is to be regarded as a solid solution.

Magnetism of Copper.—The magnetic properties of copper containing small quantities of iron is explained by J. G. Gray and A. D. Ross‡ as being due to special properties of iron when present in very dilute solid solution. This is considered to explain also the effect of heat treatment. Copper and iron are assumed to form stable chains of elementary magnets which do not, when in equilibrium, respond to the application of a magnetic field, but rapid quenching from a high temperature may break up such chains and allow the copper to assume magnetic properties.

Metallic Mirrors.—A new method for the preparation of plane metallic mirrors is described by R. Pohl and P. Fringsheim.§ The metal is placed in a magnesia crucible and heated in a good vacuum in a very small electric furnace. The vapours are condensed on a glass or quartz plate. Silver, cerium, indium, aluminium, and calcium yield

* *Annalen der Chemie*, 1912, vol. cccxc. p. 340.

† *Internationale Zeitschrift für Metallographie*, 1912, vol. iii. p. 37.

‡ *Physikalische Zeitschrift*, 1912, vol. xiii. p. 404.

§ *Berichte der deutschen physikalischen Gesellschaft*, 1912, vol. xiv. pp. 506, 546.

good mirrors, which do not require polishing, but magnesium, thallium, and the alkali metals are always deposited in crystals.

The photo-electric properties of films prepared by this method have also been studied, with the result that the region of emission is found to be displaced with time.

Optical Properties of Metals.—It is found by P. D. Foote* that the degree of polish of massive metallic mirrors affects the magnitude but not the form of the dispersion curves. The ellipticity produced in plane polarized light by reflection has also been measured. For iron, steel, and cobalt the ellipticity is negative throughout the spectrum, but for nickel and invar it changes sign within the spectrum. Heusler's alloy gives hardly any ellipticity. No evident connection has been found between the ordinary optical and electro-optical constants.

Passive Electrodes.—The periodic phenomena often observed at passive electrodes have been studied by A. Adler.† Chromium, copper, and nickel do not show periodicity, but their alloys with iron do so, and iron is therefore the cause of the intermittent passivity. The periodicity was first observed by Ostwald with chromium, but the metal used by him must have contained 1 per cent. of iron. The effect is due to local couples between active and passive areas.

Photo-Electric Properties.—The photo-electric properties of a number of metals and alloys have been examined by K. Herrmann,‡ the surfaces being smoothed by a special steel scrubber working in a high vacuum. The metals examined all show photo-electric fatigue, the rate of decay of the emission of electrons increasing with the electro-positive character of the metal. The experiments were made with aluminium, magnesium, platinum, silver, lead, and tin.

The photo-electric activity of alloys of cadmium and antimony varies in a linear manner, and the curve is therefore entirely different from that of the electrical or thermal conductivity, indicating that the electrons liberated by the action of light are not the same as the "free" electrons causing conductivity.

Present Position of the Corrosion Problem.—An editorial article on this subject§ refers to the undoubted diminution in the resistance of technical metals to corrosion in recent years, which is attributed in large part to the severe mechanical work put on metals by modern machinery. The increase in acidity of the air of large towns, and the leakage of current from conduits are contributory causes.

The literature of the subject is reviewed.

* *Physical Review*, 1912, vol. xxxiv. p. 96.

† *Zeitschrift für physikalische Chemie*, 1912, vol. lxxx. p. 385.

‡ *Berichte der deutschen physikalischen Gesellschaft*, 1912, vol. xiv. pp. 557, 573.

§ *Internationale Zeitschrift für Metallographie*, 1912, vol. ii. p. 178.

Properties of thin Metallic Films.—Thin metallic films have been prepared by V. Kohlschütter and A. Noll* by disintegrating silver cathodes in gases under low pressure, and their electrical resistance has been measured. In the order hydrogen, nitrogen, argon, increasing quantities of metal are necessary in order to obtain a film of given resistance, and this resistance subsequently changes in a manner which is characteristic for the given gas. Ultramicroscopic observations show that the degree of dispersion is greatest in argon and least in hydrogen. With time, the disperse particles unite to form larger masses, and the film becomes more transparent. If the quantity of metal is small, this change may lead to peeling. The electrical and optical properties agree.

Finely divided silver, thus prepared, oxidizes even at 100°.

Recrystallization of Lead.—The crystallization of cold-worked lead at the ordinary temperature has been studied by H. Baucke.† Just as the conversion of white into grey tin is accelerated by the presence of an electrolyte, a dilute acid may be used to accelerate the recrystallization of lead. The grain becomes coarser in several days, a maximum diameter of about 70 millimetres being then reached. A piece of lead pipe with coarsely crystalline fracture showed a great increase in size of grain after etching in dilute acetic acid, the crystals having a diagonal arrangement. Extensive growth has not been observed in ordinary sheet lead, but lead pipe shows it readily. Old lead is not specially coarse in grain. Cold-worked metal is most liable to corrosion.

Resistivity of Magnesium.—E. F. Northrup‡ has determined the resistivity and temperature-coefficient of a bar of magnesium within the temperature range 20° C. to 155° C. using the Kelvin Double Bridge method. Details are given of apparatus used and method of procedure. The resistivity of the sample, which was of a high degree of purity, was found to be $4.56_9 \times 10^{-6}$ ohm at 20° C., and the temperature-coefficient was found to be 0.00418₉.

Specific Heat of Tungsten.—Measurements of the specific heat of tungsten filaments at high temperatures, conducted by O. M. Corbino,§ show that a number of errors influence the results. The atomic heat at constant volume is 7.8.

Strain-Disease.—Some further notes on strain-disease in metals are given by E. Cohen,|| among the examples mentioned being German silver wires, the wire of an electro-magnet governing an arc lamp, and the brass holder of a glow-lamp, all of which had become brittle by

* *Zeitschrift für Elektrochemie*, 1912, vol. xviii. p. 419.

† *Internationale Zeitschrift für Metallographie*, 1912, vol. ii. p. 243.

‡ *Metallurgical and Chemical Engineering*, 1912, vol. x. pp. 277-278.

§ *Atti Reale Accademia dei Lincei*, 1912 [v.], vol. xxxi. i. p. 346.

|| *Zeitschrift für Elektrochemie*, 1912, vol. xviii. p. 616.

spontaneous crystallization after cold-working. The brass chains used to hang lamps also show the same effect very often.

Variation of the Electrical Resistance of Oxides with Temperature.—The electrical resistance of various metallic oxides as a function of temperature has been studied by A. A. Somerville.* As a rule, oxides at atmospheric temperature are non-conductors; as the temperature is increased, however, the resistance decreases until at 1000°C . most of them may be classed as conductors. The oxides in the form of powder were placed in porcelain or quartz tubes about 1 centimetre diameter and 10 centimetres long, and contact was made with the ends of the columns of oxide (about 5 centimetres long) by means of nickel rods machined to fit the tubes, 2–4 lb. pressure being applied by means of weights to the free ends of the rods. The tubes carrying the oxides were heated by a tubular resistance furnace. There is a marked similarity in behaviour between the various oxides tested in this manner, smooth curves connecting temperature and resistance being obtained in most cases.

The temperatures at which the columns of oxide each measured 10,000,000 ohms were as follows:—

	Degrees C.
ZnO	393
Fe ₂ O ₃	252
CuO (after first heating)	290
CuO (after once melted)	395
Cu ₂ O (first heating)	137 (after first heating measures 90,000 ohm at 0°)
MgO	545
MnO ₂	120
Al ₂ O ₃	?

The resistances of the oxides at the maximum temperature of the furnace 1100° were found to be as follows:—

	Ohms.
MgO	1200
Cu ₂ O, changed to (Cu + CuO) at about 800°C	
Cu ₂ O (after first heating)	18
CuO (at 1084° , its melting point)	35
CuO (after once melted)	1600
MnO ₂	70
ZnO	72
Fe ₂ O ₃	80
Al ₂ O ₃	? (infinite)

Black oxide of copper melts at 1084°C . and contracts to about half its former volume; its resistance after such treatment is greater at all temperatures.

Alumina appears to be one of the best insulators. Oxide of magnesium is also used as a non-conductor.

* *Metallurgical and Chemical Engineering*, July 1912, No. 7, vol. x. pp. 422–423.

ELECTRO-METALLURGY.

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I.—ELECTRIC FURNACES.

Electric Furnace for High Temperatures.—Constructional details of a laboratory electric crucible furnace of simple design, easily assembled and dissembled, are given by D. F. Calhane and E. E. Bard.* The furnace is 2 feet long by 11·5 inches wide by 33 inches high, and attains full heat (melting point of platinum) with an energy consumption of one kilowatt (12·5 amperes at 80 volts).

The crucible of alundum, holding 100 grammes of molten steel, rests on an alundum base, and is surrounded by a carbon resistor, in turn surrounded by an alundum tube separated by a small air space from a fireclay jacket, the whole lagged with a mixture of magnesia and asbestos, and enclosed between walls of a cement composition consisting of sand, Portland cement, and magnesia-asbestos. Particulars of a typical run show that the furnace melted 20 grammes of platinum in $1\frac{1}{4}$ hours from the start, the energy consumption being 1050 watts (15 amperes at 70 volts). The alundum refractories proved eminently satisfactory, crucibles resisting as many as twelve successive heats to the melting point of platinum without marked deterioration.

Electric Pressure Furnace.—A furnace in which materials can be heated in air or oxygen up to 100 atmospheres and 1000° is described by F. Fischer and H. Ploetze.† An unglazed porcelain tube is wound with platinum wire, very thickly insulated with magnesia, alumina, and asbestos, and is packed in a stout steel tube provided with flanges and caps, through which the heating leads, thermocouple wires, and gas inlet and outlet tubes pass through specially constructed joints. The whole furnace is immersed in water during use, in order to prevent the steel jacket from

* *Metallurgical and Chemical Engineering*, No. 8, August 1912, vol. x. pp. 461-463.

† *Zeitschrift für anorganische Chemie*, 1912, vol. lxxv. p. 1.

becoming heated. It has been found that the distribution of temperature along the tube is much less uniform under high pressures than at the ordinary pressure.

Electro-Metallurgy of Zinc.—The processes for the reduction of zinc ores in the electric furnace are described by L. Ganet.* The Scandinavian works employ the process with the object of making zinc of good quality with the cheap power available, whilst the American works mainly employ electric furnaces for the treatment of very complex ores.

An account of the Côte and Pierron process for the extraction of zinc is given by G. A. Maillet.† This process is in use at Arudy in the Basses-Pyrénées and at Ugine in Savoy. The furnace is a combined arc and resistance furnace. The lining is a conducting one, with a single electrode passing through the roof. 200 kilogrammes of ore are charged at a time, with iron turnings, and with a flux, if necessary. The vapours pass through a column of heated coke, from which the zinc emerges pure, and is condensed in the liquid form.

A furnace of 350 kilowatts, with alternating current at 55 volts, treats 1 ton of blende (35 per cent. zinc) per 95 to 100 horse-power-days. Not more than 2 per cent. of zinc remains in the slags.

Helberger Transformer Furnace.—This furnace is described by M. von Schwarz.‡ Alternating current is used, and the furnace acts as a transformer, the carbon crucible itself forming a part of the secondary circuit, contact with it being made by means of a block of a copper-silicon alloy, cooled internally by water. A fireclay casing checks loss of heat, and the burning of the crucible may be lessened by using a plumbago cylinder as a mantle. Various forms of the furnace have been constructed, from those designed for dentists, smelting 50 grammes of gold, to those taking 100 kilogrammes of metal. A temperature of 3000° may be reached, tungsten and uranium having been melted in one of the furnaces.

Using alternating current at 110 volts, the following power consumption has been observed:—

For 100 kilogrammes brass,		30 kilowatt-hours.	
„ 100	„ copper,	40-50	„ „
„ 100	„ iron,	100	„ „
„ 1	„ gold,	0.5	„ „
„ 1	„ platinum,	10.0	„ „

The loss by burning is very small, about $\frac{1}{3}$ of that in an ordinary furnace. The chief disadvantage is the destruction of the crucibles by burning, but it has been possible to melt as many as 100 charges of copper in a single graphite crucible.

* *Journal du Four électrique*, 1912, vol. xxi. p. 337.

† *Ibid.*, 1912, vol. xxi. p. 385.

‡ *Internationale Zeitschrift für Metallographie*, 1912, vol. ii. p. 258.

Small Induction Furnace.—An induction furnace suitable for lecture experiments is described by F. Fichter and G. Oesterheld.* Two primary coils are used, slipped over the ends of the transformer core. The secondary is a copper ring, 10 millimetre section and 30 millimetre diameter. Applying an alternating current at 110 volts, 30 amperes suffice to bring the ring to bright redness in 1–2 minutes.

II.—ELECTRIC SMELTING.

Electric Smelting of Zinc Ore.—A general review of the subject, and some experimental facts in connection with work at McGill University, are given by W. R. Ingalls.† Electric zinc smelting was tried by the Cowles' Brothers in 1885, and since then numerous investigators have worked on the subject. C. P. G. de Laval erected in Scandinavia in 1901 the first electric zinc smelting furnace on a commercial scale. Works were subsequently erected in Norway and Sweden, and were in operation as early as 1905. The attempts to smelt ore were for a long time not commercially successful, the product being chiefly zinc powder which had to be resmelted: any spelter produced was chiefly obtained by smelting dross, scrap, &c. Some progress was made however, and during 1911 a considerable quantity of ore was successfully smelted by a process described later.

Electric smelting is generally expected to be based on the reduction of zinc oxide, but the decomposition of sulphide of zinc by iron has been attempted as in the Côte-Pierron and Imbert-Thomson-Fitzgerald processes, the former tried experimentally at Lyon (France) in 1906, and at Arudy (Basses-Pyrénées) in 1907, apparently without success.

Early experimental work carried out by the author at McGill University, in which apparatus similar to the ordinary retort, but electrically heated, was used, confirmed the idea that if electric smelting is to offer any advantages, the process must be made continuous.

Boudouard has shown that the permissible limit of carbon dioxide in the gas of the zinc retort is very low, any excess causing oxidation of the condensing metal and formation of powder. The small size, confined character, and presence of an enormous excess of carbon in the charge are conditions which in the ordinary retort result in the carbon dioxide being kept within the necessary limits. All attempts to smelt the ore in blast-furnaces have failed owing to inability to control the percentage of the above gas. Continuous charging implies discharging of the residue as a slag that will run, a condition prohibiting any great excess of carbonaceous material, and in this important particular the continuously operated furnace differs from ordinary practice.

In his work with a continuously operated furnace the author has frequently found much higher percentages of carbon dioxide than obtain in ordinary retort practice, also quantities of carbon and ore dust in the

* *Zeitschrift für Elektrochemie*, 1912, vol. xviii. p. 429.

† *Metallurgical and Chemical Engineering*, No. 8, August 1912, vol. x. pp. 481–485.

condensers. Côte and Pierron, Johnson, and others have attempted to solve the carbon dioxide problem by such means as passing the gases through columns of incandescent carbon. Attempts at McGill University to reduce zinc oxide in a retort electrically heated externally and charged intermittently in the usual manner resulted in so slow a reduction as to offer no advantages. If, however, the charge was continuously introduced on to a bath of slag, the reduction became relatively rapid; thus a furnace with a plumbago crucible 12 inches diameter smelted 10 lb. per hour, and a furnace 18 inches \times 18 inches in horizontal section smelted 737 lb. in 23 hours. No explanation of this striking difference in the rate of reduction by the two methods is apparent.

In ordinary practice a furnace temperature of 1400° C. was once considered high; nowadays 1500° C. and upwards is reported. The conditions for low zinc retention in the residuum are a high temperature and a highly calcareous slag. Slags containing less than 1 per cent. of zinc have been made at McGill University.

Little is known at present as to the shape the smelting chamber of an electric furnace will finally take.

The operations at Trollhättan and Särpsborg were the subject of a report by F. W. Harbord in 1911. The furnaces were of the resistance type, having one large vertical electrode, the other being a carbon block bedded in the bottom of the furnace. Each furnace smelted about 2800 kilogrammes of ore in 24 hours, the products being metal and "blue powder" and oxide containing about 54 per cent. of zinc and 20 per cent. of lead. For every ton of ore smelted rather more than 2 tons of powder had to be resmelted. Difficulties in the construction of the above furnace have been indicated on account of lead, which, owing to the desirability of working at a high temperature collects as a leady spelter requiring subsequent refining. The removal, possible in most mixed sulphide ores, of the galena by gravity separation is advocated.

With regard to condensation, difficulties in this direction are to be sought not in the condenser proper, but in the character of the gas delivered to it. The attempts to condense a commercial proportion of the vapour resulting from the reduction of zinc oxide has so far failed, this being the crucial point of electric zinc ore smelting. On the basis of ore alone the consumption of power at Trollhättan was 2078 kilowatt-hours per 100 kilogrammes of ore, but for every ton of ore smelted about two tons of powder had to be resmelted. The smelting of 1000 kilogrammes of ordinary zinc ore (25–30 per cent.) is reckoned to require from 900–1000 kilowatt-hours.

The author sees no reason as yet to modify the generalizations made by him on this subject six years ago.

Electric Tin Smelting.*—Very satisfactory results are reported with the trial furnace with a capacity of about two tons of ore per day, erected in Cornwall in the year 1911.†

* *Metallurgical and Chemical Engineering*, No. 4, April 1912, vol. x, p. 241.

† *Vide Journal of the Institute of Metals*, No. 1, 1912, vol. vii, p. 287.

Electric Zinc-smelting Furnace and Notes on Electric Zinc Smelting.—Experimental facts in the attempts to produce a continuous electric zinc-smelting furnace are given by C. F. Johnson.*

The temperature at which zinc oxide is reduced is over 100° C. above the boiling point of the metal, and the vapour of zinc is very readily oxidized by carbon dioxide and steam.

The capacity of zinc retorts is still very small (50 lb.), enhancing the cost of production. In 1893 the average copper furnace smelted 50 tons of ore per day; now 500-ton furnaces are not considered large, and the celebrated Anaconda furnace smelts some 2500 tons. The cost of production has been so reduced that copper ores regarded some few years ago as good "dump-slugs" are now worked at a profit.

Similar advances have not been made with zinc; in the opinion of experts, millions of dollars' worth of complex sulphides, wasted over the dump as slag by lead and copper smelters, are waiting to be worked up.

The present process is considered to be a step in this direction.

A reverberatory resistance furnace was early abandoned for one in which the charge carried the current. The earlier types were intermittent; now a continuous process has been evolved.

The difficulties of successfully condensing the vapour have been largely overcome, the carbon dioxide formed in the smelting zone being rendered innocuous by passing the gases from the furnace through an electrically heated carbon filter, whereby the carbon dioxide is converted into the harmless monoxide.

The charge is heated to about 900° C. in a continuous pre-heater before reaching the furnace. The much dreaded "blue powder" causes but little trouble, such results as 390 lb. of metal to 11 lb. "blue powder" have been obtained. Typical slag analyses are given.

Metal as low in lead as 0.15 per cent. has been made, the usual average being 1.3 per cent. with an iron content of 0.15–1.00 per cent. in part absorbed from the condenser, which is of iron.

The unit at present is 80 kilowatts, and the process is considered to be measurably near the commercial stage.

In the second article† particulars of a 48-hours' run, described as "one of the poorest ever made with the furnace," are given by W. McA. Johnson.

	Lb. Zinc.
Ore, 2840 lb. dry at 39 per cent.	1108
Flue-dust, 3000 lb. dry at 56.7 per cent.	170
Total zinc delivered to pre-heater	1278
	Lb. Zinc.
Zinc in spelter, 691 lb. at 97.1 per cent.	670
" "blue-powder," 32 lb. at 96.0 per cent.	30.8
" flue-dust, 280 lb. at 68.6 per cent.	192.0
" slag, 1359 lb. at 2.49 per cent.	34.0
" charge not melted and found in furnace, 81 lb. at 50.5 per cent.	20.7
Total zinc accounted for	947.5

* *Metallurgical and Chemical Engineering*, No. 5, May 1912, vol. x. pp. 281–283.

† *Ibid.*, No. 9, September 1912, vol. x. pp. 537–538.

Analyses of slags gave the following results:—

	Per Cent.
SiO ₂	27.5-39.2
FeO	14.3-27.9
Zn	1.90-3.5
ZnO	2.38-4.31
Pb and Cu	less than 0.05

Approximate composition of the ore, per cent.:—

	Per Cent.
Zn	39.0
Pb	8.7
Fe	12.0
CaO	5.2
MgO	1.0
SiO ₂	8.0
K ₂ O, Na ₂ O	3.0
Cu	0.59
S	3.7
	Hours.
Time of smelting	48
Total kilowatt-hours	2340
Kilowatt-hours per pound spelter	3.39
„ „ ton pay charge	1490

III.—ELECTRO-DEPOSITION.

Aluminium Cathode.—C. W. Bennett* proposes the use of an aluminium tube, 10 inches long and 1 inch in diameter, as a rotating cathode in the electrolysis of copper solutions. It may be rotated at any speed up to 6000 revolutions, and carry a current up to 300 amperes. The copper cylinder after deposition is merely slotted, and is then readily peeled off the aluminium surface. At a high temperature, the copper obtained has the strength and ductility of the annealed metal, but if the solution is cooled and well stirred, copper of “hard-drawn” quality is obtained. The current efficiency is very high (99.6 per cent.) in acid sulphate solutions. Bronze and brass have not been deposited satisfactorily.

Electro-deposited Metals.—The surfaces of a number of electrically deposited metals are described and photographed by B. Wäser and E. H. Schulz. †

Influence of Colloids on the Deposition of Lead.—H. Freundlich and J. Fische ‡ have examined the influence of a number of colloids on the quality of lead deposited from solution by means of electrolysis. The order of activity of the colloids compared does not agree with that

* *Journal of Physical Chemistry*, 1912, vol. xvi. p. 287.

† *Elektrochemische Zeitschrift*, 1912, vol. xix. pp. 36, 63.

‡ *Zeitschrift für Elektrochemie*, 1912, vol. xviii. p. 885.

observed in their influence on colloidal gold. The results seem to indicate that the colloid is absorbed by the metal, that the velocity of crystallization is diminished, and that the density and compactness of the metal is thereby increased. The influence of the colloids is the same when lead is precipitated from its solution by zinc instead of being electrolyzed.

ANALYSIS AND PYROMETRY.

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I.—ANALYSIS.

Analysis of White Metals.—A complete scheme for the analysis of white metals is proposed by R. Kopenhagen.* The alloy is boiled with nitric acid and evaporated to dryness. The residue is dissolved in nitric acid and ammonium nitrate, and boiled. The deposit, which contains the tin and antimony with some copper, lead, and iron, is washed with ammonium nitrate, and then mixed with a large excess of ammonia, a current of hydrogen sulphide being passed, dissolving the tin and antimony, whilst the residual sulphides are dissolved in nitric acid and bromine and added to the main solution.

The ammonium sulphide solution is evaporated to dryness, and then evaporated with hydrochloric acid and potassium chlorate, after which the residue is dissolved in hydrochloric acid with the addition of ammonium oxalate, and the antimony is precipitated by means of hydrogen sulphide. The liquid is boiled, and the precipitate is collected and washed with strong oxalic acid solution to which ammonium sulphate and hydrochloric acid have been added.

The precipitated antimony sulphide is heated with potassium hydroxide solution, filtered, and the antimony precipitated from the filtrate by hydrochloric acid, brought into solution, and estimated by the iodine method.

The tin in the filtrate is estimated by electrolysis, the lead as sulphate; the zinc and iron are separated by means of ammonia, the iron then being estimated volumetrically and the zinc as sulphide. Copper is estimated electrolytically in a separate sample.

Assay of Ores containing Metals of the Platinum Group.—

A. C. Dart † gives details of method employed in assaying platinum-bearing ore from the Rambler Mine, Wyoming. The precious metal

* *Annales de Chimie analytique*, 1912, vol. xvii. p. 241.

† *Metallurgical and Chemical Engineering*, 1912, vol. x. pp. 219-220.

buttons from cupellation are parted with 12 per cent. nitric acid and finally with concentrated nitric acid in test-tubes placed in boiling water. Silver, palladium, and platinum are dissolved, leaving the gold. Silver is precipitated from the nitric acid solution by means of hydrochloric acid. Metallic palladium and platinum are then separated from the solution by reduction with formic acid. The mixed palladium and platinum are then dissolved in aqua regia, and the platinum separated as ammonium platinic chloride, from which the metallic platinum is obtained by slow ignition.

Assay of Small Quantities of Platinum.—Buttons containing small quantities of platinum, obtained in the assay of ores or bullion, may be treated as described by F. P. Dewey.* The button is parted with nitric acid, which dissolves both silver and platinum. The solution is diluted, and a very dilute solution of hydrogen sulphide is added. The precipitate, which contains the platinum with some silver, is burnt and cupelled, and the bead is then parted by means of sulphuric acid.

Atomic and Weight Percentages.—A mathematical proof of the geometrical construction for converting atomic percentages into percentages by weight, or *vice versa*, is given by E. Jänecke.† The method may be applied to ternary as well as to binary systems. In another paper, F. Hoffmann,‡ urges the general adoption of atomic percentages in place of percentages by weight in all metallographic investigations, on account of the greater theoretical clearness, and of the readiness with which intermetallic compounds may be detected. It is easy, with the geometrical constructions now available, to convert such figures in such a way as to obtain the percentages by weight required for practical purposes.

Copper in Pyrites.—The tedious removal of aqua regia by evaporation is avoided, according to W. D. Treadwell,§ by adding ammonia to the solution until just turbid, followed by 8 to 12 grammes Rochelle salt, 5 grammes ammonium sulphate, and 20 c.c. of strong ammonia, for 3 or 4 grammes pyrites. The cold solution is then electrolyzed with a rotating cathode which must be completely immersed. With a potential of 2 volts, deposition is complete in 1 to $1\frac{1}{4}$ hours.

Estimation of Antimony in its Alloys with Lead.—It is proposed by K. Friedrich|| to estimate small quantities of antimony in lead by determining the freezing point. The method has been in use by H. Beckmann for the last six years in an accumulator factory. A quartz mercury thermometer is used, which may conveniently have in addition to the scale in degrees a special scale showing directly the percentage of antimony up to 10 per cent. Actual experiments show that the instru-

* *Chemical News*, 1912, vol. cvi. p. 8.

† *Metallurgie*, 1912, vol. ix. p. 320.

‡ *Ibid.*, p. 324.

§ *Chemiker-Zeitung*, 1912, vol. xxxvi. p. 961.

|| *Metallurgie*, 1912, vol. ix. p. 446.

ment is perfectly trustworthy to 6 per cent. of antimony. The accuracy of the thermometer is not affected by repeated heating and cooling. The instrument is plunged into the molten lead at about 350°, and the lead is stirred until a distinct arrest of the mercury column takes place.

Estimation of Antimony in White Metal.—An electrolytic method is described by I. Compagno.* A platinum-iridium cathode, roughened in a sand-blast, is bent into the form of an open cylinder, and provided with slits for the circulation of the liquid. The alloy is dissolved in nitric and hydrochloric acids, and the solution is then rendered alkaline with sodium hydroxide, with the addition of sodium sulphide and potassium cyanide. It is then boiled, cooled, and electrolyzed with a platinum wire anode. The cathode deposit of antimony obtained overnight is washed with water without interrupting the current, and finally with alcohol.

Estimation of Chromium in Bronzes.—Chromium in bronzes containing tin and antimony may be estimated, according to H. Schilling,† by dissolving in aqua regia, evaporating with sulphuric acid until white fumes appear, and boiling with water. Copper and antimony are then removed by digestion with iron wire, and the filtrate is diluted, treated with a few drops of silver nitrate as a catalyst, and oxidized with ammonium persulphate. After boiling, a little hydrochloric acid is added, the solution is cooled, and the chromic acid titrated with ferrous sulphate.

Platinum Alloys.—H. Arnold‡ proposes to dissolve the alloy in aqua regia, and evaporate the residue repeatedly with hydrochloric acid, dissolve in hydrochloric acid, and precipitate as potassium platinichloride. The washed and dried precipitate is heated in hydrogen until reduced, and is then warmed first with dilute nitric acid, and then with ammonia, to remove any silver chloride, and the residual platinum is ignited and weighed. The other metals are estimated in the filtrate.

Ternary Systems.—The theoretical study of ternary systems has been continued by N. Parravano and A. Sirovich,§ who have now dealt with systems in which a gap of miscibility occurs in the liquid as well as in the solid state.

Quaternary Systems.—Continuing their theoretical studies of quaternary systems, N. Parravano and A. Sirovich|| show that the construction of the diagram is relatively simple when neither compounds nor solid solutions are formed, when the geometrical peculiarities of the tetra-

* *Atti Reale Accademia dei Lincei*, 1912 [v.], vol. xxi. i. p. 473.

† *Chemiker-Zeitung*, 1912, vol. xxxvi. p. 697.

‡ *Zeitschrift für analytische Chemie*, 1912, vol. li. p. 550.

§ *Gazzetta chimica italiana*, 1912, vol. xlii. i. p. 577.

|| *Ibid.*, p. 333.

hedral model have been mastered. A number of diagrams are given illustrating the authors' method of construction.

II.—PYROMETRY.

Amalgam Thermometers.—For work at temperatures down to -60° , D. McIntosh and F. M. A. Johnson * have found that thermometers filled with a liquid amalgam containing 8.5 per cent. of thallium are very suitable. The readings of such an instrument are directly proportional to those of the platinum thermometer.

Radiation Pyrometry.—Five articles dealing with this subject have been published by G. A. Shook.†

1. *Radiation Laws.*—Laboratory methods of measuring high temperatures and temperature scales are briefly dealt with, followed by a discussion of radiant energy, the best physical conception of which is given by the electron hypothesis. According to this latter we must regard the chemical atom or molecule as consisting of a nucleus of positive electricity in equilibrium with particles of negative electricity or "electrons," whose mass has been found to be about $\frac{1}{1836}$ th part of the mass of an atom of hydrogen. On heating a body it is the motion of these electrons into or out of the atom which produces radiation, and not the motion of the atom itself. Transverse waves are set up in the ether, which are transformed into heat whenever the disturbance strikes a material body.

The reflection, transmission, and absorption of heat, and black body properties are dealt with, and experimentally determined curves are given showing the energy distribution of a black body for various temperatures; and it is seen how for low temperatures the energy maximum is far out in the invisible red shifting towards the shorter wave-lengths as the temperature rises, at the same time the relative amount of radiation in the visible spectrum becomes much greater than at lower temperatures, this being the reason why a metallic filament lamp which can be run at a high temperature is so much more efficient than a carbon lamp.

Proof is given that the interior of a uniformly heated enclosure radiates like a black body, and the laws of Stephan and Boltzman and a simplified equation expressing Wien's "distribution law" are given.

2. *Theory of Radiation Pyrometers.*—Radiation Pyrometers may be of two classes, in the first of which black body temperature is determined by measuring the total energy radiated, and in the second some particular wave-length is selected, and the measurement of temperature made by adjusting to equality two photometric fields produced by a standard source and the body whose temperature is to be measured. As examples

* *Journal of the American Chemical Society*, 1912, vol. xxxiv. p. 910.

† *Metallurgical and Chemical Engineering*, April 1912, vol. x. No. 4, pp. 238-240; 334-338; No. 7, 416-420; No. 8, 478-481; No. 9, 534-535.

of the first class, in which the Stephan-Boltzman law is used, the Fery and Thwing pyrometers are described with the aid of diagrammatic sketches of the instruments. Fery has recently introduced a more robust type of instrument in which the temperature is measured by means of a minute expansion spiral of two dissimilar metals instead of a thermocouple. As the Bureau of Standards have lately been able to make extremely minute thermocouples of antimony and bismuth by a very ingenious method, a "bank" of these couples might be used with these radiation pyrometers, giving a much greater sensitivity at low temperatures. Passing on to the second class, or Optical Pyrometers, four essential features of construction of these instruments are considered in some detail—

(a) The sensitive photometric screen.

Two of the most sensitive of these screens, the Lummer Brodhun cube and the Brace prism, have never as yet been applied.

(b) The method of varying the intensity of the incident radiation.

(c) The production of monochromatic light.

(d) The standard lamp.

The Wanner, Le Chatelier, Holborn-Kurlbaum (probably the most sensitive pyrometer now in use), and the Morse Thermo-Gauge instruments are described with the aid of diagrammatic sketches.

(3) *Calibration of Radiation Pyrometers.*—Black body standards, data required for calibration and limits of accuracy of total radiation and optical pyrometers are discussed. As a standard of comparison for industrial work, the wide filament carbon incandescent lamp whose black body temperature for various currents has been determined, is advocated in preference to the amyl acetate flame, which is unreliable and troublesome.

Except in the case of a few metals, such as platinum and palladium, very little is known at present as to the departure from black body radiation when true black body conditions are not realized, as, for example, in the determination of the temperature of an incandescent sheet of metal.

(4) *Determination of very High Temperatures.*—The laws of Planck and Wien are discussed, and it is shown that for temperatures up to 3000° C. Wien's law is sufficiently accurate, but that for higher temperatures Planck's law should be used.

The method of extending the scales of radiation pyrometers by the use of absorption mirrors and glasses, sectorized discs, polarizing prisms, &c., and the consequent changes in the temperature equations, are discussed.

(5) *Relation between Black Body Temperature and True Temperature.*—When a temperature observation is made on a stream of molten iron, for example, the value obtained is always somewhat lower than the true temperature. If the metal is in the interior of a furnace, however, the true temperature is obtained. The author gives two tables of corrections to be applied in connection with the above phenomena in the case of several metals in order to obtain the true temperature.

FURNACES AND FOUNDRY METHODS.

Historical Note on Electric Furnaces.—Thirty years ago Siemens melted 20 lbs. of steel in an electric furnace with which he had been experimenting since 1878. This was the first practical application of the electric furnace, for, although other investigators had made some use of electro-thermic methods, their source of energy was the voltaic cell, whereas Siemens obtained his power from electric generators.*

Laboratory Crucible and Muffle Furnaces for High Temperature Work.—Constructional details, character of materials used, &c., of injector crucible and muffle furnaces of comparatively simple design for use in laboratory tests up to a temperature of 1600° C., are given by M. A. Verneuil.†

The mixture of gas and air under pressure is so introduced as to give the flame a spiral motion round the crucible wall in the one case, and in the space between the wall and the muffle jacket in the other.

In the case of the crucible furnace a temperature of 1530° C., measured by means of a thermocouple, was attained with a gas consumption of about 50 cubic feet per hour, and an air-pressure of less than 4 lbs. per square inch.

Losses in the Melting of Brass.—Experiments are described by F. Bensele,‡ with the object of avoiding the loss of zinc which always occurs in the melting of brass. Attempts to prepare zinc by melting blende with copper in an electric furnace failed, the brass usually containing only 16 per cent. or less of zinc, whilst large quantities of zinc passed into the matte. Melting zinc and copper together in a closed arc furnace failed, owing to the high pressure developed, but better results were obtained by the use of a resistance furnace. A globular iron vessel, lined with fireclay, is provided with a central carbon resistance rod, and can be rolled on its axis to facilitate mixing. In making 20 kilogrammes of 70 30 brass, 1·96 kilowatt-hours were required for melting after the furnace was once heated. It is calculated that, on a larger scale, the preparation of 100 kilogrammes of brass, assuming that 15 charges could be worked in a day, would consume 16 kilowatt-hours.

* *Engineer*, July 5, 1912, vol. cxiv. p. 13.

† *Bulletin de la Société d'Encouragement*, June 1912, vol. cxvii. pp. 792-802.

‡ *Metallurgie*, 1912, vol. ix. p. 523.

Melting Point of Fire Bricks.—An investigation has been made by C. W. Kanolt* at the Bureau of Standards on the melting point of certain fire bricks and refractory materials. The determinations were made in a vacuum resistance furnace.

The following table is given:—

Material.	Melting Point. Degrees C.
Fireclay brick	1555–1725 (mean 1649)
Bauxite brick	1565–1785
Silica brick	1700–1705
Chromite brick	2050
Magnesia	2165
Kaolin	1735–1740
Bauxite	1820
Bauxite clay	1795
Chromite	2180
Alumina (pure)	2010
Silica (pure)	1750

The figure for silica does not represent the true melting point, but the temperature at which the silica flows distinctly.

Refractories.—The materials alundum,† crystolon, magnesia, and lime are dealt with by F. A. J. FitzGerald.‡

Alundum.—There are two forms of this material made by purifying and fusing bauxite in the electric furnace, white and brown, the former being the purer, and having a melting point of 2050° to 2100° C., that of the brown being not more than 50° lower. Linear coefficient of expansion—white, 78×10^{-7} ; brown, 85×10^{-7} . Heat conductivity much higher than fire brick, specific gravity 3.9 to 4.0, has so far been applied chiefly to laboratory apparatus (crucibles, muffles, combustion boats, tubes, &c.). It is believed that an excellent pyrometer tube can now be manufactured; these tubes are more refractory than any porcelain or fireclay tube, and have the important advantage that their heat conductivity is distinctly higher. An experimental furnace roof of alundum bricks withstood 40–50 heats at temperatures which destroyed a roof of silica brick in 5 to 6 hours. Used as a roofing in a steel furnace, they failed to come up to expectations, although the temperature was considerably lower, exhibiting a tendency to break off in layers, analyses indicating that this was due to the action of lime and magnesia vapours rising from the basic slag.

Crystolon (Silicon Carbide).—Two forms, crystalline (commonly called carborundum) and amorphous. A typical sample of the latter showed on analysis—

	Per Cent.
Silicon	69.41
Carbon	29.18
Iron and aluminium	0.59

* *Metallurgical and Chemical Engineering*, No. 9, September 1912, vol. x. p. 533.

† *Ibid.*, March 1912, vol. x. [iii.] pp. 129–132.

‡ See also a paper by L. E. Saunders to the American Electro-Chemical Society (*Transactions*, 1911, vol. xix. p. 333), and a previous article, *Metallurgical and Chemical Engineering*, April 1911, vol. ix. [iv.] pp. 225–226.

Articles of crystolon are made by moulding the powdered carbide mixed with a binding agent, such as glue or dextrine, to the desired shape, and heating them in an electric furnace to the temperature of formation of the carbide, whereby a very strong refractory article is obtained. The coefficient of expansion is less than that of silica, and the heat conductivity higher than that of alundum. Thus comparative tests of the heat conductivities of crystolon, alundum, and silica showed that at 435° C., for example, crystolon bricks transmitted 79 per cent. more heat than alundum bricks, and 117 per cent. more than silica.

The electrical conductivity of crystolon is considerable; bonded with a little clay, however, this is largely reduced. Thus measurements at 20° C. gave a value for resistivity (centimetre cube) of 318×105 , and at 1040° C. of 4×105 .*

Tested in an experimental steel furnace as a roofing material in a manner similar to the alundum, no appreciable reaction between lime vapours and crystolon was found. Its refractoriness is remarkable; thus in one furnace heated to an excessively high temperature a good grade of fire brick used as a heat lagging outside the crystolon was completely melted down by the heat transmitted by the crystolon without in any way damaging the latter.

Magnesia.—The tendency of this material to crack when heated to high temperatures can be removed by calcining it, short of actually melting it, at electric furnace temperatures, whereby its power of absorbing carbon dioxide is at the same time practically destroyed.

Lime.—The properties of lime fused in an electric furnace have been studied. It is a better conductor of heat than ordinary lime, and stands heat followed by sudden cooling very well. Slaking is a process of days instead of hours.

Transformer Crucible Furnace.—The Allgemeine Elektrizitäts Gesellschaft of Berlin has recently placed on the market transformer crucible furnaces taking charges from 1–100 kilogrammes.† In these furnaces the secondary current from the transformer passes through the crucible forming the resistor, which is the only part subjected to wear, and can be readily renewed.

* No units are given, and the figures appear to be incorrect. Inquiries are being made from the author.—ED.

† *Metallurgical and Chemical Engineering*, August 1912, No. 8, vol. x. p. 501.

STATISTICS

Consumption of Molybdenum.—It is stated by the Canadian Department of Mines * that several tons of molybdenum are consumed annually by the iron and steel works of the United States alone, simply as a chemical reagent for analytical work.

Molybdic acid is used for colouring porcelain, and in the dyeing industry.

By far the greatest part of molybdenum consumed, however, is used in the production of special alloy steel.

Copper Production in the United States.—The smelter production of primary copper in the United States in 1911 † was the largest in the history of the country, amounting to 1,097,232,749 lbs., an increase of about $1\frac{1}{2}$ per cent. over that of 1910.

Arizona, Montana, Michigan, and Utah were the largest producers.

Copper Production in Japan.—The total output of copper in Japan ‡ during 1911 was 51,708 tons, valued at £2,791,588, showing an increase of 2562 tons over the production of this metal during 1910. More than half the total output comes from three principal mines.

Mineral Output of German Africa.—The following figures are extracted from the official report of the German Colonial Office for the year ended 31st March 1911: §—

Country.	Material.	Value.
German East Africa . . .	{ Gold ore, { 7,333 tons.	Fine gold, £46,400
Togoland	{ Iron ore, { 400 tons.	£3,540
German South-West Africa	{ Copper ore, { 36,500 tons.	...

* *Engineer*, April 12, 1912, vol. cxiii. p. 379.

† *Metallurgical and Chemical Engineering*, July 1912, No. 7, vol. x. p. 398.

‡ *Board of Trade Journal*, August 1, 1912, vol. lxxviii. p. 296.

§ *Ibid.*, April 25, 1912, vol. lxxvii. p. 200.

Malaysian Tin Exports.—The Federated Malay States Government *Gazette* * publishes the following table showing the weight of tin (tin exported as ore is taken at 70 per cent. of the gross weight of the ore) exported from the Federated Malay States during 1910 and 1911 (1 picul = 133½ lbs.):—

States.	1910.		
	Tin.	Tin contained in Tin Ore.	Total.
	Piculs.	Piculs.	Piculs.
Perak	109,867	311,468	421,325
Selangor	43,397	196,795	240,192
Negri Sembilan	121	34,576	34,697
Pahang	12,930	27,744	40,674
Total	166,315	570,583	736,898
	1911.		
	Tin.	Tin contained in Tin Ore.	Total.
	Piculs.	Piculs.	Piculs.
Perak	97,835	339,504	437,339
Selangor	54,215	176,960	231,275
Negri Sembilan	90	29,140	29,230
Pahang	15,281	28,673	43,954
Total	167,421	574,277	741,698

Mineral Output, Union of South Africa.—The South African Mines Department, † in their report for 1911, give the total value of the mineral output for the year 1911 as £47,679,294, as compared with £43,674,249 in 1910.

The total values of some of the items are given below.

	1910.	1911.
	£	£
Gold	31,991,295	35,049,041
Silver	90,790	98,507
Coal	1,867,220	1,935,153
Copper	477,381	552,145
Tin	326,352	411,871
Zinc	3,020	291
Lead	669	344

These figures show an increase in value for 1911 as compared with 1910, except in the cases of zinc and lead.

* *Metallurgical and Chemical Engineering*, April 1912, No. 4, vol. x. p. 226.

† *Board of Trade Journal*, October 24, 1912, vol. lxxiv. p. 192.

The gold production of the Rand Mines is still increasing. The coal produced from the Transvaal coalfields alone is valued at more than half of the total output of the Union.

Copper mining in Natal is almost at a standstill on account of difficulties of transport.

Mineral Production of Ontario.—The Ontario Bureau of Mines * have issued statistics of the production of certain minerals in that province during the first six months of 1912, from which the following values have been abstracted :—

	January-June 1911.		January-June 1912.	
	Quantity.	Value, ¹ Dollars.	Quantity.	Value, ¹ Dollars.
Gold (ounces)	2,276	42,320	11,854	235,198
Silver (ounces)	15,231,969	7,644,200	14,258,403	7,936,600
Nickel (metric tons) . .	8,418	1,809,759	10,179	2,166,895
Copper (metric tons) . .	4,418	631,827	5,170	736,469
Cobalt and nickel } Oxides, &c. . . } (lbs.)	219,584	64,876	854,324	192,073

¹ Dollar=4s. 1½d.

Mineral Production of Western Australia.—In their report for the year 1911, the Department of Mines of Western Australia† give the following figures for the total output of the materials enumerated during 1910 and 1911 respectively :—

	1910.		1911.	
		£		£
Coal (tons)	262,166	113,699	249,890	111,154
Copper ore (tons)	6,309	27,271	9,825	33,709
Copper ingot and metal (tons) .	1,281	68,657	828	44,409
Gold (ounces)	1,470,632	6,246,848	1,370,868	5,823,075
Silver (ounces)	176,139	18,777	169,043	18,333
Lead ore (tons)	248	1,433	1,549	15,002
Tin ore and ingot (tons) . .	500	45,129	495	55,220
Wolfram (tons)	2	190	9	826
Zinc (tons)	12	147	12	189

Russian Copper Industry.—The copper and iron industry of Russia is reported ‡ to be improving considerably owing to the enterprise of the Nedyi Syndicate, which keeps in touch with about 90 per cent. of the Russian copper producers.

* *Board of Trade Journal*, October 3, 1912, vol. lxxix. p. 31.

† *Ibid.*, October 31, 1912, vol. lxxix. p. 254.

‡ *Ibid.*, October 24, 1912, vol. lxxix. p. 193.

The following figures show the increase in the amount of copper smelted during the first seven months of 1912, as compared with the corresponding period of 1911 :—

	First 7 Months of 1911.	First 7 Months of 1912.	Increase. ¹
	Pouds.	Pouds.	Per Cent.
Urals	441,000	636,000	44·2
Caucasus	256,000	336,000	31·2
Siberia	122,000	151,000	23·8
At chemical works and refineries .	31,000	42,000	35·5
Total	850,000	1,165,000	37·2

¹ 1000 pouds=about 16 tons.

Silver Production of the World.—In Parliamentary Papers Sydney Buxton * estimates the world's production of silver for 1911 at 224,000,000 fine oz., valued at £24,800,000.

Tungsten Ore.—The production of tungsten ore † in the United States of America has not been recorded previous to 1900, the output being insignificant. Since 1906 the production expressed in short tons of 60 per cent. tungstic acid content has been as follows :—

1906	928
1907	1640
1908	671
1909	1619
1910	1821

The Metallurgy of Tin in 1910-11.—According to H. Men-
nicke, ‡ the price of tin in London rose from £147 per ton in January 1910 to £206 in December 1911. The production in 1910 amounted to—

	Tons.
Straits shipments	57,500
England	17,855
Banka sales in Holland	13,631
Germany	11,295
Australia	8,700
Billiton sales in Holland and Java	2,240

The largest consumers were the United States (49,900 tons), England (21,100 tons), and Germany (18,100 tons).

The recovery of tin from tinplate scrap is increasing, but the electrolytic method is now little used, and the large works all employ chlorina-

* *Engineer*, May 24, 1912, vol. cxiii. p. 541.

† *Metallurgical and Chemical Engineering*, April 1912, No. 4, vol. x. p. 255.

‡ *Elektrochemische Zeitschrift*, 1912, vol. xix. pp. 31, 67, 98, 126, 158.

tion. Of these, the most important are the firm of T. Goldschmidt, Essen, and the French and American companies of the same name. A second American plant is in course of erection, and there is also a work for the process in Sydney.

The improvements in the metallurgical processes for the reduction of zinc ores are also described.

Platinum in America.—Two American States, California and Oregon, produced platinum in 1911,* the former to the extent of 511 oz., and the latter 117 oz., total value 18,138 dollars.

Tinplate in America.—The output of tinplate mills in America † has shown a rapid increase in the past two decades. In 1892 the total output was 18,803 tons, in 1900 this had risen to 302,665 tons, and in 1910 it reached 725,000 tons, making America the world's chief producer.

World's Metal Statistics.—The *Metall Gesellschaft* ‡ publish the following particulars in their statistics for the year 1911 :—

Metal.	Year.	Production, Tons.	Consumption, Tons.	Average Price. £.	Stocks on Jan. 1, 1912. Tons.
Copper. . . {	1909	846,700	783,900	58 17 3	175,100
	1910	877,600	911,100	57 3 2	148,500
	1911	898,400	944,800	56 1 9	102,100
Tin . . . {	1909	108,600	105,600	134 15 6	23,120
	1910	115,700	121,300	155 6 2	20,300
	1911	118,200	117,400	192 7 0 $\frac{3}{4}$	19,580
Lead . . . {	1909	1,085,600	1,080,500	13 1 8	...
	1910	1,132,900	1,115,700	12 19 0	...
	1911	1,117,800	1,133,100	13 19 2 $\frac{1}{2}$...
Zinc . . . {	1909	783,200	798,900	22 3 0	...
	1910	816,600	820,600	23 0 0	...
	1911	895,400	900,500	25 3 2	...
Nickel . . {				per kilo	
	1910	20,100	...	0 3 2 $\frac{1}{4}$...
	1911	24,500	...	0 3 2 $\frac{1}{4}$...
Aluminium {	1910	43,800	44,200	0 1 5 $\frac{1}{4}$...
	1911	46,700	47,900	0 1 2 $\frac{1}{4}$...

* *Metallurgical and Chemical Engineering*, October 1912, No. 10, vol. ix. p. 659.

† *Ibid.*, April 1912, No. 10, vol. x. p. 255.

‡ *Engineer*, July 12, 1912, vol. cxiv. p. 38.

Metal Consumption by the Leading Countries.

Country.	Year.	Consumption (Tons).			
		Lead.	Copper.	Zinc.	Tin.
United States	1909	345,200	319,800	246,900	42,800
	1910	372,800	339,900	244,500	49,900
	1911	358,200	321,900	353,300	48,000
Germany	1909	213,200	179,400	188,100	17,100
	1910	210,400	200,400	191,600	18,200
	1911	229,700	225,800	219,800	19,300
United Kingdom	1909	202,700	108,300	155,500	17,800
	1910	208,400	146,000	177,800	21,100
	1911	199,400	159,400	175,700	18,400
France	1909	102,300	73,400	66,900	7,300
	1910	89,800	85,700	56,300	7,300
	1911	99,000	95,000	82,000	7,400

The total production of copper in 1911 shows an increase over that of 1910, but the increase is only very slight when compared with those of 1909-10 and 1908-9. The stagnation of the copper industry in America is held to be partly responsible for this fact, but prospects indicate a recovery during the present year (1912).

The world's consumption of copper in 1911 experienced a greater development than did its production. This excess of consumption is traceable largely to European markets. The consumption of copper in the United States, on the other hand, was less in 1911 than in 1910.

The production of lead in 1911 shows a decrease of 15,100 tons on the figure for 1910; this is attributed more particularly to the smaller Spanish output.

The consumption of lead, however, rises decidedly from 1910-11, and the increase in price of both copper and lead during the present year is ascribed to this disproportion between supplies and consumption.

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[A carefully written review of the field of electrometallurgy.]

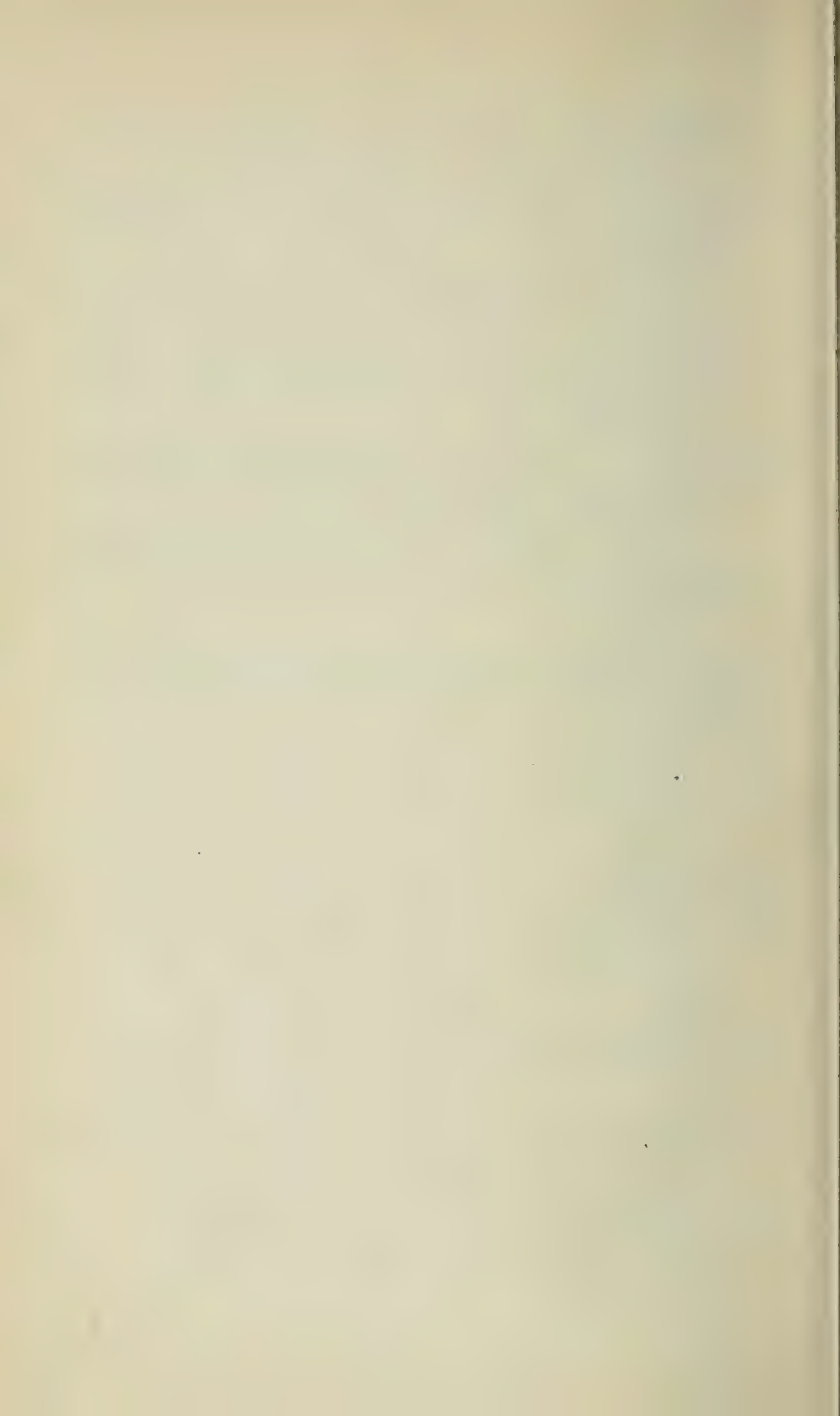
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[The various chapters of the book deal with the following:—Generalities and methods, preparation of specimens, methods of examination, constituents, diagrams, qualitative analysis, general constitution of metals, study of the principal constituents of alloys, quantitative analysis of steel, copper, lead, zinc, tin, nickel, manganese, aluminium and precious metal alloys, physical state and disposition of elements, slags, precipitates and powders. The book is of an essentially practical nature.]

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[A book by a practical man, dealing with the facts of electro-plating and the composition and handling of baths giving good results, with a chapter on the influence of colloids in metal plating, and a 30-page chapter on the deposition of alloys.]

[Owing to unforeseen circumstances the Abstracts are not as complete as had been intended, but the missing Abstracts will appear in the next Volume.—ED.]



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INSTITUTE OF METALS.

Founded 1908. Incorporated 1910.

To the Secretary,

I, the undersigned....., being of the required age and desirous of becoming aMember of the INSTITUTE OF METALS, agree that I will be governed by the regulations of the Association as they are now formed, or as they may be hereafter altered, and that I will advance the interests of the Association as far as may be in my power; and we, the undersigned, from our personal knowledge, do hereby recommend him for election.

Name in full.....

Address.....

Business or Profession.....

Qualifications.....

.....

Signature.....

Dated this.....day of....., 191 .

.....
.....
.....

Signatures
of three
Members.

The Council, having considered the above recommendation, present Mr.....to be Balloted for as a.....Member of the INSTITUTE OF METALS.

To be filled up
by the
Council.

CAXTON HOUSE,
WESTMINSTER, S.W.,

Chairman.

Dated this.....day of.....191.....

[FOR QUALIFICATIONS OF MEMBERS, SEE SECTION 1, OTHER SIDE.]

(It would be a convenience if the Candidate's Card were sent with this form.)

EXTRACTS FROM THE RULES.

(MEMORANDUM AND ARTICLES OF ASSOCIATION.)

SECTION I.—CONSTITUTION.

Rule 4.—Members of the Association shall be either Honorary Members, Fellows, Ordinary Members, or Student Members.

Rule 5.—*Ordinary Members* shall be more than twenty-three years of age, and shall be persons occupying responsible positions. They shall be:—

either (a) persons engaged in the manufacture, working, or use of non-ferrous metals and alloys;

or (b) persons of scientific, technical, or literary attainments connected with or interested in the metal trades or with the application of non-ferrous metals and alloys.

Student Members shall be more than seventeen years of age, and shall not remain Student Members of the Association after they are twenty-five years of age, and shall be:—

either (a) Students of Metallurgy;

or (b) pupils or assistants of persons qualified for ordinary membership whether such persons are actually members of the Association or not.

Student Members shall not be eligible for election on the Council nor entitled to vote at the Meetings of the Association.

SECTION II.—ELECTION OF MEMBERS.

Rule 6.—Applications for membership shall be in writing in the form marked "A," and such application must be signed by the applicant and not less than three members of the Association.

Rule 7.—Such applications for membership as Ordinary Members or Student Members as are approved by the Council shall be inserted in voting lists. These voting lists will constitute the ballot papers, and will specify the name, occupation, address, and proposers of each candidate. They shall be forwarded to the members for return to the Secretary at a fixed date, and four-fifths of the votes recorded shall be necessary for the election of any person.

Every such election shall be subject to the payment by the applicant of his entrance fee and first annual subscription, and he shall not become a member of the Association nor be entered on the Register of Members until such sums are actually received from him. In the event of his failing to pay such sums within the time specified in the notification to him of his election, his election shall be void.

Rule 8.—Upon election under the preceding Article the Secretary shall forward to the applicant so elected notice thereof in writing in the form marked "B."

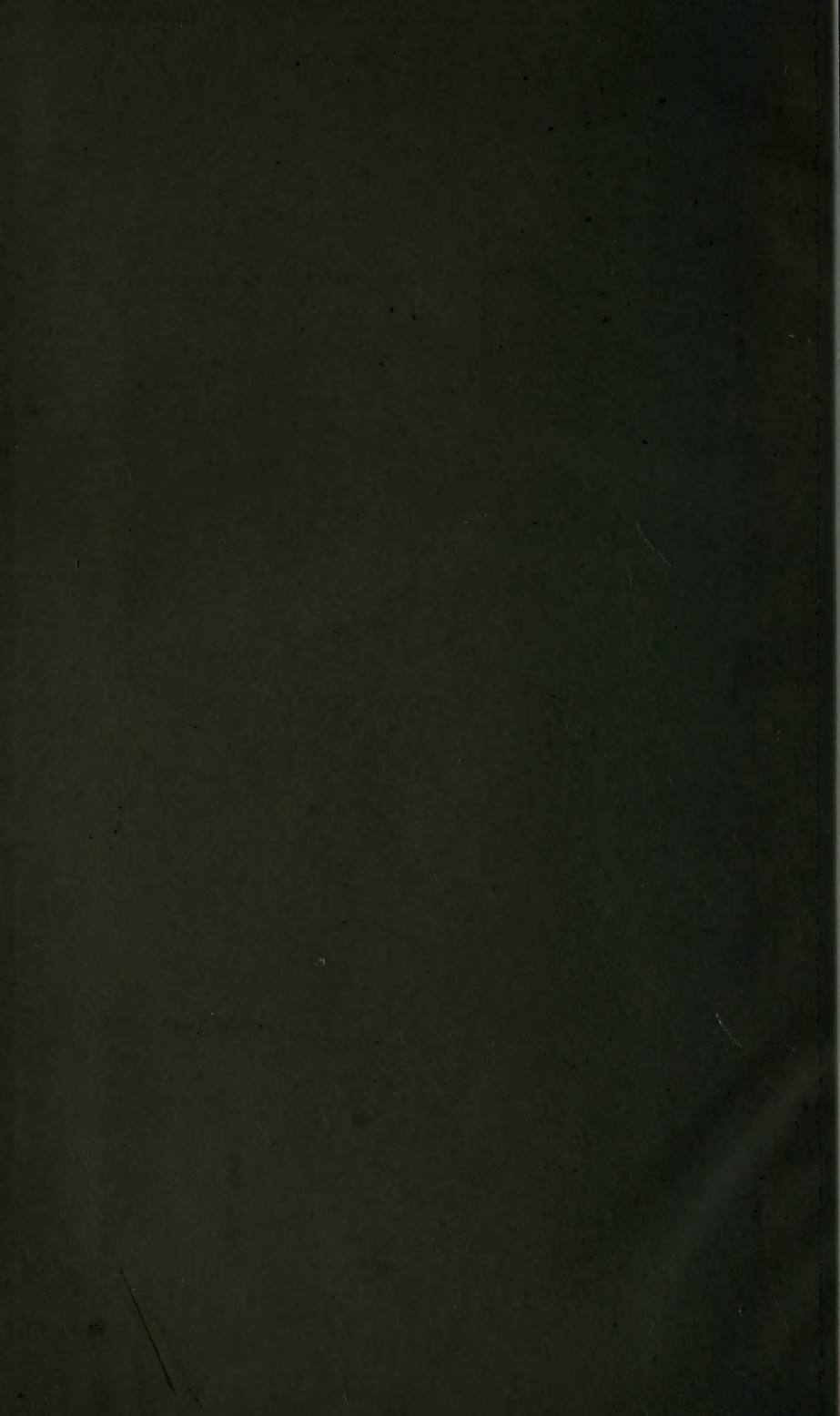
Rule 9.—In the case of non-election, no mention thereof shall be made in the minutes.

SECTION VI.—SUBSCRIPTIONS.

Rule 28.—The subscription of each Ordinary Member shall be two guineas per annum, and of each Student Member one guinea per annum. Ordinary Members shall pay an entrance fee of two guineas each, and Students an entrance fee of one guinea each.

Rule 29.—Subscriptions shall be payable in advance on July 1st in each year, save in the case of Ordinary Members and Student Members elected under Clauses 6 and 7 hereof, whose entrance fee and annual subscription shall become payable in accordance with the notification to them of their election. Every subscription shall cover the period down to the 30th of June next following, and no longer.

Rule 30.—Subject to the provisions of Clause 7 hereof, any member whose subscription shall be six months in arrear, shall forfeit temporarily all the privileges of the Association. Due notice on the form following marked "C" shall be given to such member, and if such subscription remains unpaid upon the date specified for payment in this notice, the Council may remove such member from the Register of Members of the Association, and thereupon any member whose name is so removed shall cease to be a member thereof, but shall nevertheless remain liable to the Association for such arrears.



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